Supporting Information

Multiple H-bonds Induced Mechanically Robust Vat Photopolymerization 3D Printing Poly(urethane-urea) Elastomers

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1. Experimental Section

1.1 Materials

Polytetramethylene ether glycol (PTMEG, M_n = 1000 g/mol and M_n = 2000 g/mol), 4,4′-methylenediphenyl diisocyanate (HMDI, 99%), N, Ndimethylacetamide (DMAc, 99.8%, Extra Dry, Water ≤ 50 ppm), dibutyltin dilaurate (DBTDL, 95%), hydroxypropyl acrylate (HPA, 98%), polyetheramine (D230, 98%), and dibutyltin dilaurate (DBTDL) were purchased from Energy Chemical. Ethyl (2,4,6-trimethylbenzoyl) phenylphosphinate (TPO-L, 95%) was purchased from Shanghai Guangyi Chemical Co., Ltd. All the reagents were used as received without further purification. Pancreatin (Biosharp), CCK-8 (Invigentech, Cat. No. IV08-100), Horse serum (Biological Industries, Cat. No. 04-007-1A), MEM medium (Corning, Cat. No. 10-010CV) were received and used without further purification. Deionized (DI) water was made in the laboratory.

1.2 Synthesis of HMDI-PUU$_{1000}$ and HMDI-PUU$_{2000}$ elastomers

The synthetic routes for the HMDI-PUU$_{1000}$ and HMDI-PUU$_{2000}$ polymers are shown in **Figure S1**, and the details are as follows. PTMEG was vacuum heated at 120 °C and stirred for 3 h to remove moisture. Dry PTMEG (10 g, PTMEG$_{1000}$, 20 g, PTMEG$_{2000}$, and 10 mmol) and HMDI (5.91 g, 25 mmol) were placed in a three-neck round bottom flask equipped with a mechanical stirrer, and DBTDL (0.1 g, 0.2 mmol) dissolved in N,

N-dimethylacetamide (DMAc, 10 mL for HMDI-$PUU_{1000,}$ 30 mL for HMDI-PUU_{2000}) was added to the flask. The reaction system was further heated at 80 °C under a N_2 atmosphere and stirred for 3 h, followed by cooling to room temperature. D230 (1.15 g, 5 mmol) as the chain extender, dissolved in DMAc (50 mL for HMDI-PUU_{1000}, 30 mL for HMDI-PUU_{2000}), was added to the reaction system, which was further kept at 30 °C for 4 h under stirring and a N_2 atmosphere. The reaction was monitored through FTIR measurements, and when the absorption of isocyanate groups no longer decreased, the mixture of HPA (9.1 g 35 mmol, HPA excess ensured that the -NCO was consumed.) was added to the system. The reaction was heated to 70 °C until the absorption of isocyanate groups on the FTIR spectrum disappeared. Finally, a viscous and transparent acrylic terminal polymer solution was obtained.

1.3 Characterization

The ^{1}H-NMR (400 MHz) spectra were measured on a Bruker 400 MHz spectrometer by using DMSO-d_6 as the solvent. The molecular weights of the polymers were measured using gel permeation chromatography (GPC, Agilent 1260 II) with tetrahydrofuran (THF) as the mobile phase at a flow rate of 1 mL min^{-1}. Fourier transform infrared spectroscopy (FT-IR) was performed at room temperature on a Bruker TFS-66 v/s FT-IR spectrometer. The resolution was 32 scans, and the scan range was between

4000-400 cm^{-1}. To obtain variable temperature FTIR spectra in-situ, the film sample was secured to a stretching bench and subjected to a temperature increase from 30 to 160 °C. The absorption spectra were recorded in the wavenumber range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}, utilizing 32 scans at a heating or cooling rate of 1°C min^{-1}. Additionally, the spectra obtained at different temperatures were normalized using the stretching peaks of methylene. The acquired FTIR absorption spectroscopic data was processed using two-dimensional correlation spectroscopy (2D-COS) software to generate correlation spectra. Prior to analysis, the spectra were baseline corrected and smoothed. The correlation peaks were visualized using contour maps, with red indicating positive intensities and blue indicating negative intensities. The transmittance of the films was determined using a UV-vis spectrophotometer at wavelengths ranging from 800 to 400 nm. Liquid samples were tested on potassium bromide window sheets coated with film (ϕ = 25). Thermogravimetric analysis (TGA) was performed on an instrument (Netzsch STA 449F5, Germany) in the temperature range from room temperature to 800 °C at a heating rate of 10 °C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry (DSC) of the samples was performed on a NETZSCH DSC 200 F3 (Germany). All the samples were subjected to an N_2 flow rate of 50 mL min^{-1} using a TA Instruments Q200

differential scanning calorimeter operating at a heating/cooling rate of 10 °C min^{-1}, where the second heating scan was considered the real scan.

1.4 Preparation of the photopolymer. The composition of the poly(urethane-urea) precursors with different oligomers was composed of 10.0 g of photosensitive monomer and 0.15 g of photoinitiator. Then, the mixture was stirred vigorously at 500 rpm for 15 min in the dark until the photoinitiator was completely dissolved. Finally, the photosensitive resin was obtained after the resin was vacuumed for 10 min to eliminate air bubbles.

1.5 UV curing of polyurethane elastomer film. The photopolymer resins were poured into a PTFE mold (100 mm×100 mm×8 mm) and then subjected to UV box curing (light intensity of 10 mW cm^{-2}, 405 nm) for 120 s.

1.6 3D printing of polyurethane elastomers. In this work, we utilized a DLP 3D printer (Yantai Runchuang Industrial Technology Co., Ltd, China) equipped with a 405 nm light source to fabricate the polyurethane elastomer parts (printing temperature: 25-30 °C). The layer thickness was set at 50~100 μm to facilitate rapid processing, with exposure time and intensity parameters set at 10-15 s. During the printing process, a light pattern was projected onto the liquid photopolymer resin, selectively solidifying it. After each layer was completed, the printing platform

ascended by one layer thickness, followed by projection of a new pattern onto the resin for curing. This process was repeated for each layer until the objects were fully printed. Subsequently, the samples were cleaned with ethanol and underwent UV box curing (at a light intensity of 10 mW cm^{-2}, 405 nm) for 60 s to complete the postcuring process.

1.7 The conversion of double bonds. Real-time ATR-FTIR analysis was employed to track the conversion of double bonds at approximately the 812 cm^{-1} peak under 405 nm UV irradiation with a UV-LED light (10 mW cm^{-2}, 405 nm). The ester carbonyl absorption peak (C=O) at 1725 cm^{-1} in the FTIR spectrum can be used as an internal standard. The conversion rate of the double bond was calculated by the following equation:

$$DC = 1 - \frac{(A_V/A_C)t}{(A_V/A_C)t_0} \quad (1)$$

where Av and Ac are the areas of the stretching vibration peaks of the vinyl group and carbonyl group, respectively, and DC is the conversion rate of the double bond.

1.8 Rheology and Photo Rheology Measurements: The viscosity of the resins was assessed using a rheometer (HAAKE, RS6000, Germany) at shear rates ranging from 0.1 to 100 s^{-1} at 25 °C. The measurement was carried out with two 35 mm diameter stainless steel plates, and a loading gap of 400 μm was employed for viscosity testing. Additionally, a rheometer was employed to investigate the UV-curing reaction kinetics of

the resins. The UV-curable resin was exposed to 10 mW cm^{-2} of UV irradiation for 200 s to determine the energy storage moduli (G′) and loss moduli (G″). Viscosities were tested at the shear rate of 100 s^{-1}. The shear storage (G′) and loss (G″) moduli were measured at frequency of 1 Hz and the shear stress at 10 000 Pa. The temperature during the test was increased from 0 to 80 °C (the heating rate was 0.1 °C min^{-1}).

2. Mechanical Properties Testing

The tensile tests were performed on a universal testing machine (EZ-S, Shimadzu, 500 N) in accordance with ASTM D68-14 at room temperature. The samples were cut into dumbbell shapes (the test size was 12 mm × 2.0 mm × 0.5 mm) for testing. The stretching rate was set at 50 mm min^{-1}. At least five individual tensile tests were performed for each kind of sample. The true stress (σ_t) and true strain (ε_t) are calculated based on the engineering stress-strain curves via the following equation:

$$\sigma_t = \sigma(1+\varepsilon)$$
$$\varepsilon_t = ln(1+\varepsilon) \quad (2)$$

where σ is the engineering stress, L is the instant length of the deformed specimen, L_0 is the original length of the specimen, and Ɛ is the engineering strain.

The tensile toughness of the samples can be defined by integrating the area under the engineering stress–strain curves measured at a stretching speed

of 50 mm min^{-1} using the following equation:

$$\text{Toughness} = \int_{\varepsilon = 0}^{\varepsilon = \varepsilon_{max}} \sigma d\varepsilon \tag{3}$$

For the cyclic tensile test, both loading and unloading processes were performed at a strain rate of 50 mm min^{-1} at room temperature. The cyclic deformation treatment was continued until the final cycle, at which point the targeted final strain was reached. In addition to the different strain cycles described above, the samples were stretched to 100%, 200%, and 300% strain for 100 cycles.

Cyclic loading-unloading tensile tests were performed to investigate the energy dissipation mechanism of the elastomer sample. The dissipated energy (U_{hys}) and energy loss coefficient (η) were calculated by the following equations:

$$U_{hys} = \int_{\varepsilon = 0}^{\varepsilon = \varepsilon_x} (\sigma_{load} - \sigma_{unload}) d_\varepsilon \tag{4}$$

$$U = \int_{0}^{\sigma_{max}} (\sigma_{load} - \sigma_{unload}) d_\varepsilon \tag{5}$$

$$\eta = \frac{U_{hys}}{U} \tag{6}$$

where σ_{load} and σ_{unload} are the corresponding stress during loading and

unloading, respectively, and U denotes the elastic energy stored in materials at the time of stretching to the maximum stress σ_{max}.

Fracture energy tests were conducted via tensile tests using a single-edge notched sample (with a notch length of 1 mm). The notched and unnotched specimens (gauge length of 10 mm, width of 5 mm, and thickness of 0.8 mm) were both tested at a stretching speed of 50 mm min^{-1}. The fracture energy (G_c) was calculated by the following equation:

$$G_c = \frac{6wc}{\sqrt{\lambda_c}} \tag{7}$$

where c represents the length of the slit (1 mm), λ_c represents the elongation at break of the notched sample, and w represents the strain energy calculated by integration of the stress-strain curve of the unnotched specimen until εc ($\varepsilon_c = \lambda_c - 1$). Both the loading and unloading processes for the cyclic tensile tests were measured at a rate of 50 mm min^{-1}.

3. Cell Proliferation and Cytotoxicity Assay

3.1 Cell Viability Assessment.

The polyurethane elastomer samples were sterilized via ultraviolet irradiation for 30 minutes. Subsequently, the sterilized samples were immersed in a culture solution at a concentration of 3 cm^2 mL^{-1} for extraction. Next, the samples were incubated at 37 °C with 5% CO_2 for a period of 24 h to prepare the extraction solution for use. The cell viability was assessed using a cell counting kit-8 (CCK-8) following the

manufacturer's protocol. In brief, L929 cells were seeded into 96-well plates at a density of 6 × 103 cells per well and incubated at 37 °C with 5% CO_2 overnight. Subsequently, various concentrations of extraction solution (1 mg/ml, 3 mg/ml, 5 mg/ml, 7 mg/ml, and 9 mg/ml) were added for further incubation. The culture medium was aspirated after incubation for 1, 2, and 3 days, followed by three washes with phosphate-buffered saline (PBS). Subsequently, 20 μL of CCK-8 solution was added to each well of a 96-well plate, and the cells were then cultured at 37 °C for 2 h. The absorbance at a wavelength of 450 nm was measured using a microplate reader (SPARK 10 M, TECAN, Switzerland) was used. Each experiment was performed three times.

The blank group was wells without medium and cells, and the control group was a medium with only cells without samples. The measured optical density (OD) values of the blank group, control group, and experimental group were coded as OD_{bla}, OD_{con}, and OD_{exp}, respectively. And the cell survival rate was calculated as follows:

$$cell\ viability = \frac{OD_t - OD_{nc}}{OD_{pc} - OD_{nc}} \times 100\% \quad (8)$$

The preparation follows a 9:1 ratio of MEM medium to serum. L929 cells are cultured in a 5% CO_2, 37°C constant temperature incubator. The samples are subjected to ultraviolet irradiation for 30 minutes on both sides, then soaked in complete medium. After being placed in a 5% CO_2,

37°C incubator for 24 h, they are filtered through a 0.22 um membrane for later use. The experiment is divided into two groups: Control and Sample 1. The Control group receives 1mL/well of complete medium, while Sample 1 receives 1mL/well of a 7 mg/ml sample working solution, with each group represented by one well. Harvest logarithmically growing L929 cells, perform cell counting, adjust the cell concentration, and seed at a density of 6×10^{-4} cells/well into confocal dishes. Incubate these under 5% CO_2 at 37°C until the cells adhere. Following the aforementioned grouping and treatment protocols, culture for 1, 2, or 3 days. Subsequently, dilute reagent A (Calcein-AM) and reagent B (PI) 10-fold using dye dilution solution. Mix the diluted reagents with serum-free medium, and wash with PBS. Add 1mL of staining solution per well, incubate in the dark at room temperature for 15 minutes, and then observe and photograph. The green (492 nm) and red (545 nm) fluorescence of the cells was observed using a fluorescence microscope (Olympus, FV1200). Each experiment was performed three times.

3.2. Anticoagulant Properties:

(a) Activated partial thromboplastin time (APTT): The instrument automatically aspirated 0.1 mL of plasma and 0.1 mL of actin reagent (prewarmed to 37 °C, composed of brain phospholipid, 1×10^{-4} M tannic acid, buffer solution, stabilizer, and preservative) and thoroughly mixed

them. The mixture was then incubated at 37 °C for 3 minutes. Subsequently, 0.1 mL of 25 mM $CaCl_2$ solution was aspirated from the instrument, the solution was thoroughly mixed, and the timer was started. Simultaneously, the instrument detected clot formation. **(b)** Prothrombin time (PT): The instrument automatically aspirated 0.1 mL of plasma into a testing cup, which was then incubated at 37 °C for 1 minute. Subsequently, 0.2 mL of Thromborel S reagent (prewarmed to 37 °C, prepared from freeze-dried human placental coagulation enzyme (≤60 g/L) and 1.5 g/L $CaCl_2$) was aspirated from the instrument and thoroughly mixed before starting the timer. The instrument then measured the coagulation time. **(c)** Thrombin time (TT): The instrument automatically aspirates 0.1 mL of plasma into the test cup, incubates at 37 °C for 1 minute, and then aspirates 0.2 mL of coagulation time determination reagent (prewarmed to 37 °C, composed of freeze-dried bovine thrombin at approximately 1.5 IU/mL and buffer solution) after thorough mixing, timing begins, and the instrument detects the clotting time. **(d)** Plasma fibrinogen (FIB): The instrument automatically aspirated 0.1 mL of plasma into the test cup, incubated at 37 °C for 1 minute, and then aspirated 0.05 mL of fibrinogen test reagent (prepared from freeze-dried bovine thrombin preparation (approximately 100 IU/L), stabilizer, and buffer solution) for thorough mixing. All the above values were calculated by the instrument. The

testing equipment: a rotary mixer (Thermo Scientific, USA), an automatic coagulation analyzer (CS-5100, SYSMEX), a multifunctional microplate reader (Varioskan Flash, Thermo Scientific, USA), and a constant temperature incubator (ZRD-A5210, Zhicheng, Shanghai). Healthy human plasma for standard blood transfusion was supplied by Hangzhou Yanqu Information Technology Co., Ltd. in China.

3.3 Hemolysis Ratio: First, 0.2 mL of volunteer erythrocytes was mixed with 1.0 mL of 0.9% NaCl solution in a centrifuge tube, followed by centrifugation of the solution for 10 minutes. The supernatant was then collected and combined with 0.25 mL of saline for later use. The resulting sample was transferred to a 1.5 mL centrifuge tube and washed with 1.0 mL of 0.9% NaCl solution. Subsequently, 20 μL of the red blood cell suspension was added to the tube and incubated at 37 °C for 60 minutes. After incubation, the sample was centrifuged at 3000 r/min for 5 minutes, and 0.2 mL of the supernatant was transferred to a 96-well plate. The absorbance at 545 nm was then measured using a microplate reader. Negative and positive controls were included, with the negative control consisting of 20 μL of red blood cell suspension mixed with 1 mL of normal saline and the positive control consisting of 20 μL of red blood cell suspension mixed with 1 mL of tridistilled water. The process for each sample and control was repeated three times. The relative hemolysis rate

of the sample red blood cells was calculated using the following formula:

$$hemolysisrat = \frac{D_t - D_{nc}}{D_{pc} - D_{nc}} \times 100\%$$

(9)

where D_t was the absorbance of the experimental sample, D_{nc} was the absorbance of the negative control group, and D_{pc} was the absorbance of the positive control group. The human blood experiment involved in this experiment was conducted at Yanxuan Biotechnology (Hangzhou) Co., Ltd. and approved by the Experimental Animal Ethics Committee of Yanxuan Biotechnology (Hangzhou) Co., Ltd.

3.4 Statistical analysis: Three parallel trials of solvent extraction and tensile tests were conducted. The data were obtained with OriginPro software and are presented as the mean values ± standard deviations (SD).

4. Supplementary Figures and Tables

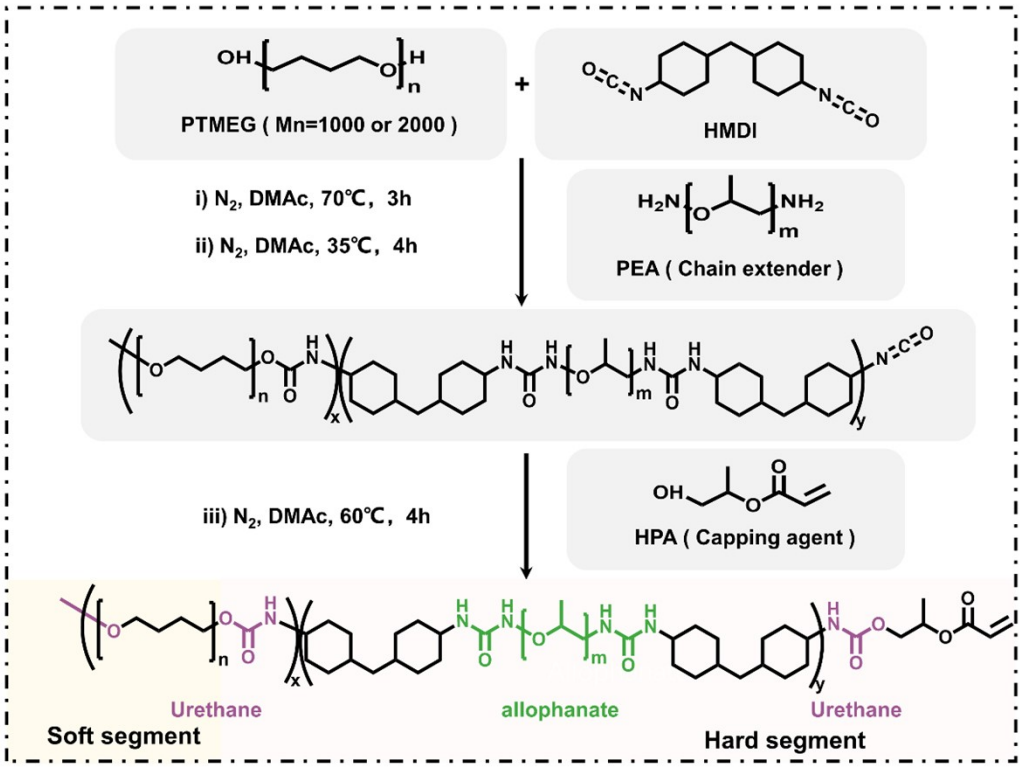

Figure S1. Synthesis of HMDI-PUU oligomers.

Table S1. Parameters of the physical properties of the elastomers

Samples	Mw (g/mol)	Mn (g/mol)	Ww/Mn	Tg [°C]	Decompose 5% [°C]
HMDI-	27520	8294	3.3	17.6	278.1

PUU_{1000}					
HMDI-PUU_{2000}	34199	16998	2.0	5.2	283.7

Table S2. Summary of the mechanical properties of the HMDI-PUU elastomers.

Samples	Ultimate engineering stress [MPa]	Elongation at break [%]	Toughness [MPa]
HMDI-PUU_{1000}	19.5±3.3	465.1±46%	29.3±7.4
HMDI-PUU_{2000}	28.3±1.1	754.6±37%	57.9±4.2

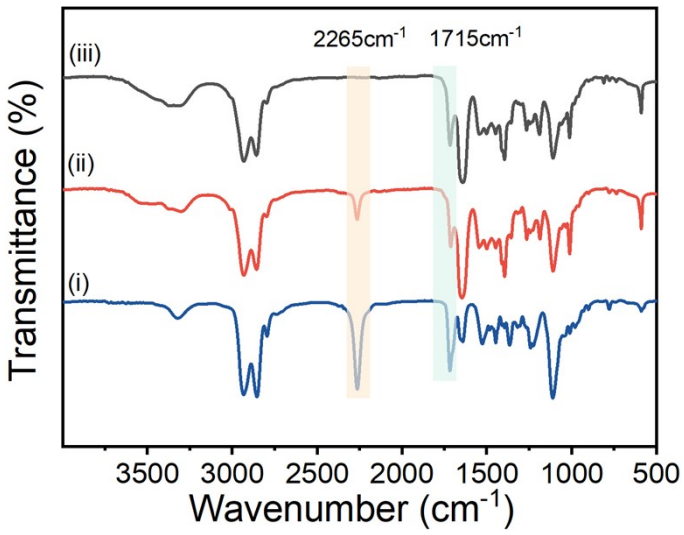

Figure S2. FTIR spectrum of HMDI-PUU$_{1000}$ during synthesis.

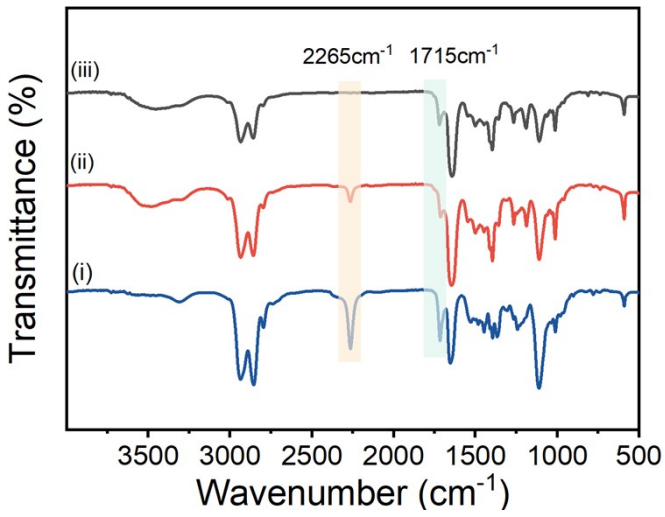

Figure S3. FTIR spectrum of HMDI-PUU$_{2000}$ during synthesis.

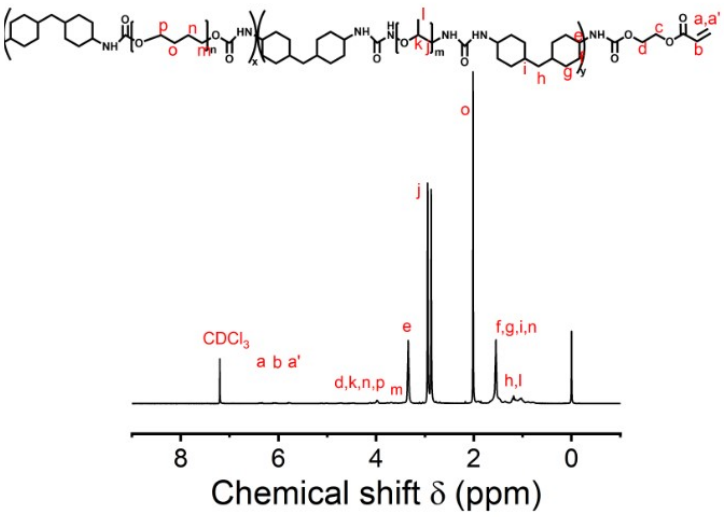

Figure S4. ^{1}H NMR spectrum of HMDI-PUU$_{1000}$ in Chloroform-d. ((400 MHz, Chloroform-d) δ 3.39 (d, J = 5.6 Hz, 1H), 2.93 (s, 2H), 2.07 (s, 2H), 1.63-1.58 (m, 1H).)

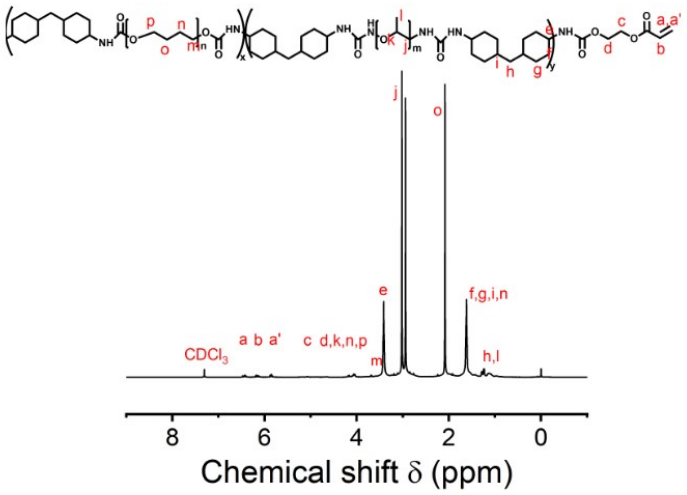

Figure S5. ^{1}H NMR spectrum of HMDI-PUU$_{2000}$ in Chloroform-d. ((400 MHz, Chloroform-d) δ 7.26 (s, 1H), 3.39-3.34 (m, 35H), 2.97 (s, 46H), 2.89 (s, 45H), 1.59-1.55 (m, 33H), 1.19 (d, J = 6.1 Hz, 3H).)

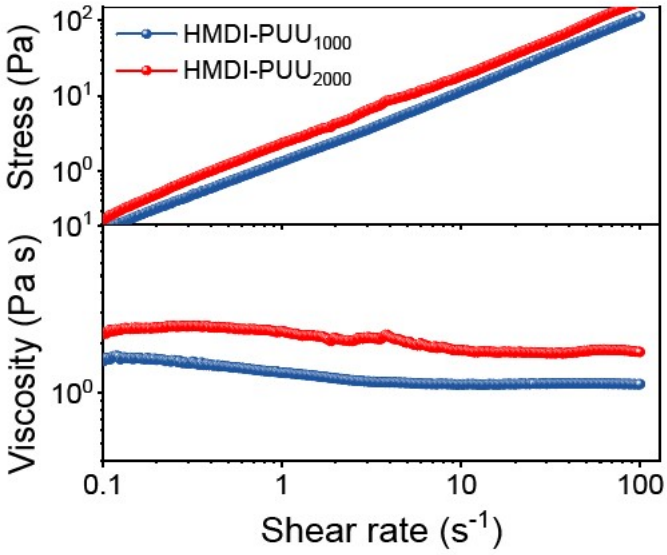

Figure S6. Viscosity of photosensitive resins.

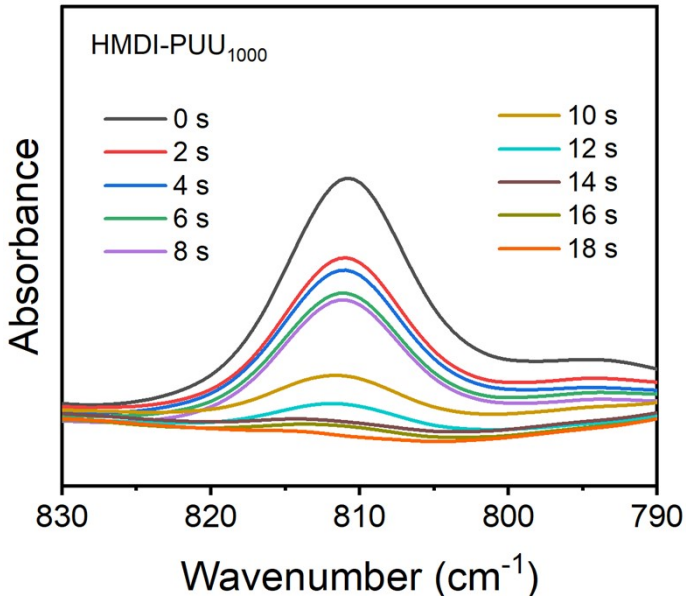

Figure S7. ATR-FTIR absorption spectra of the HMDI-PUU_{1000} resin were recorded under UV irradiation.

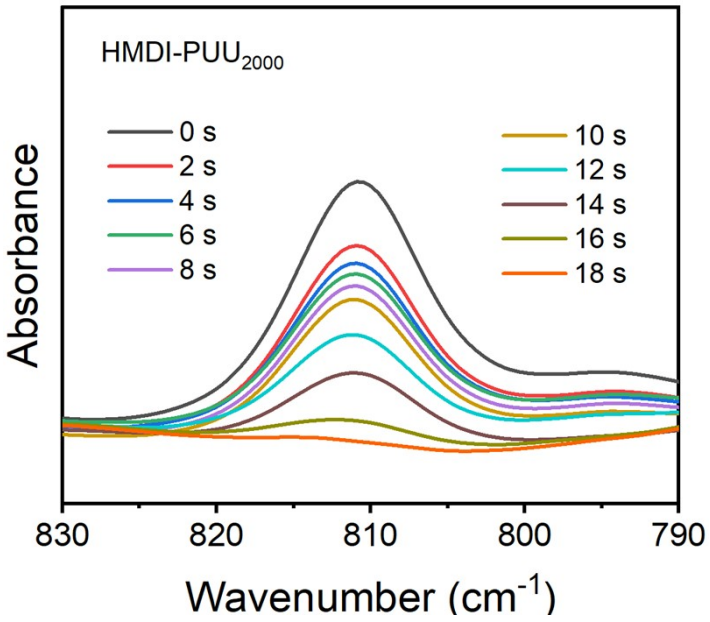

Figure S8. ATR-FTIR absorption spectra of the HMDI-PUU_{2000} resin were recorded under UV irradiation.

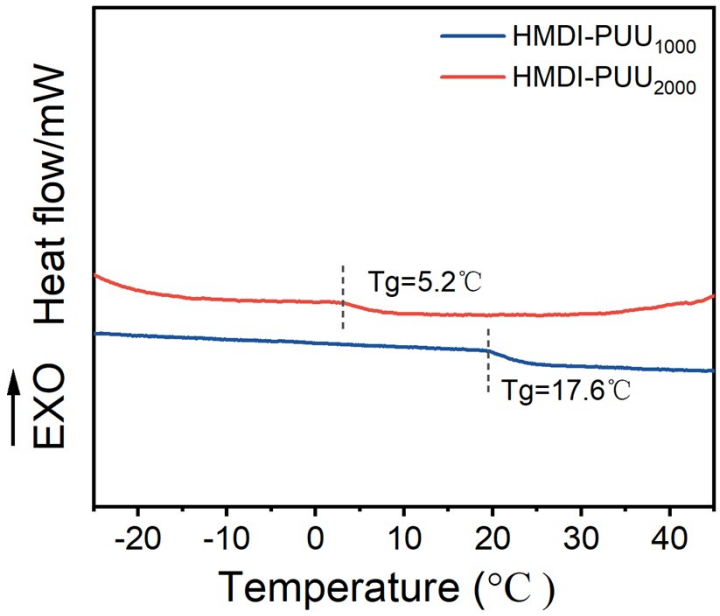

Figure S9. DSC heating curves of the HMDI-PUU_{1000} and HMDI-PUU_{2000} elastomers.

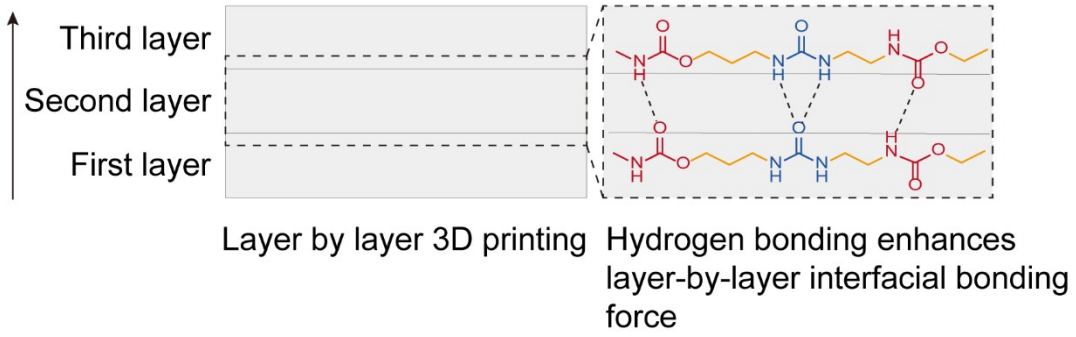

Figure S10. Hydrogen bonding interactions enhance interfacial bonding in layer-by-layer 3D printing.

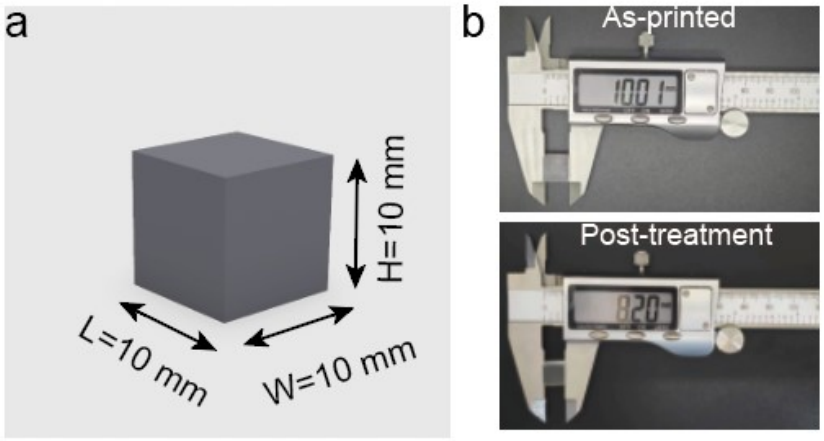

Figure S11. Statistical dimensional analysis after solvent removal. (printed slice model with actual sample photographs).

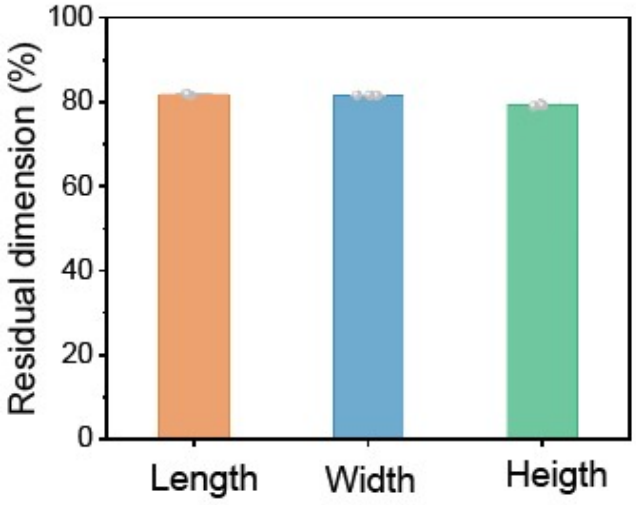

Figure S12. Three identical cube samples were printed. The residual size is calculated as the ratio of the final size (after solvent removal) to the initial size (before solvent removal). The results indicate that after solvent removal, shrinkage in all three dimensions is highly consistent. After annealing the printed part, the dimensions shrinkage in three dimensions is approximately 19.2%. It can be found that the dimensional shrinkage is isotropy and the difference among three dimensions is less than 2.5%.

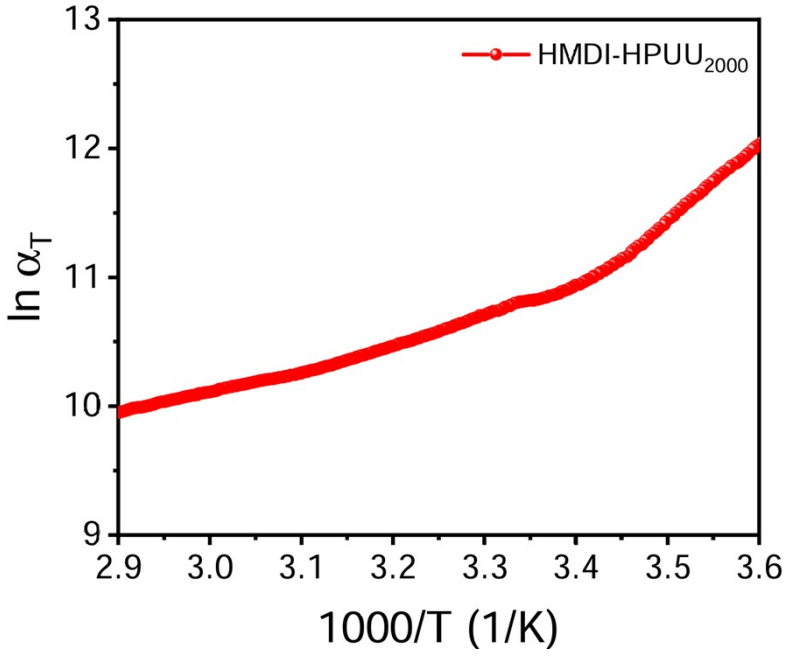

Figure S13. ln α_T-1/T curves of the HMDI-PUU_{2000}.

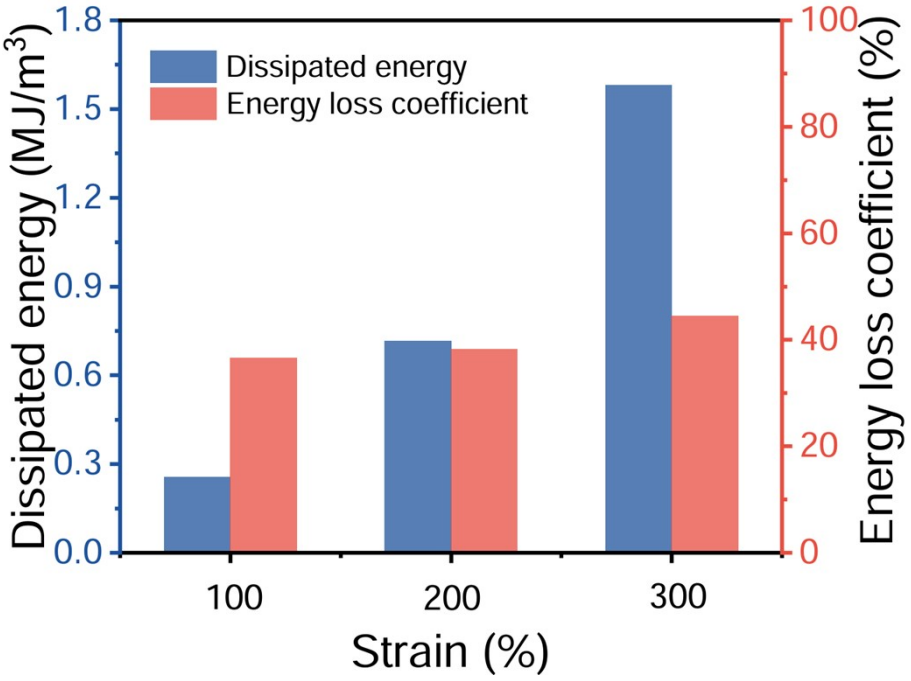

Figure S14. Dissipated energy and energy loss coefficient of HMDI-PUU_{2000} at different strains.

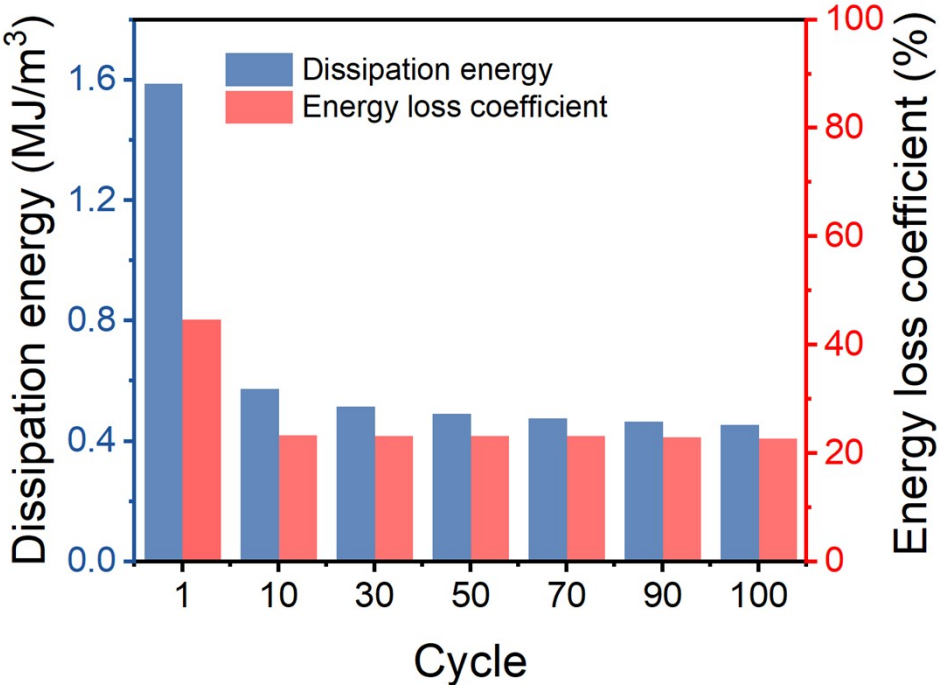

Figure S15. Calculated dissipation energy and energy loss coefficient for

cycle numbers ranging from 1 to 100.

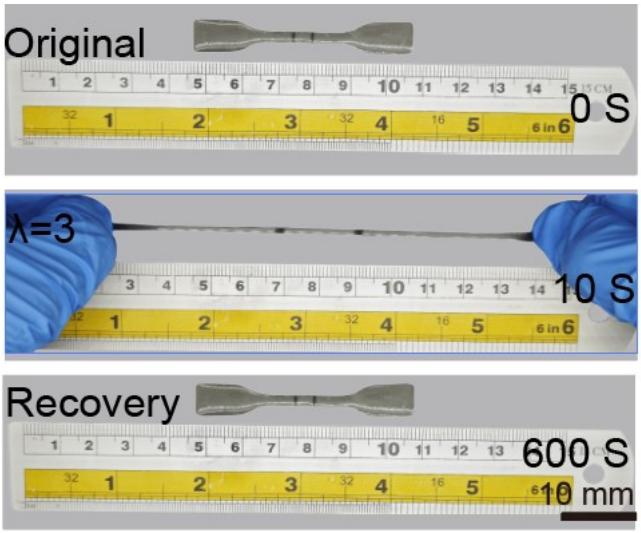

Figure S16. Digital images of an HMDI-PUU$_{2000}$ film that was restored to its original length after being stretched to 300% strain.

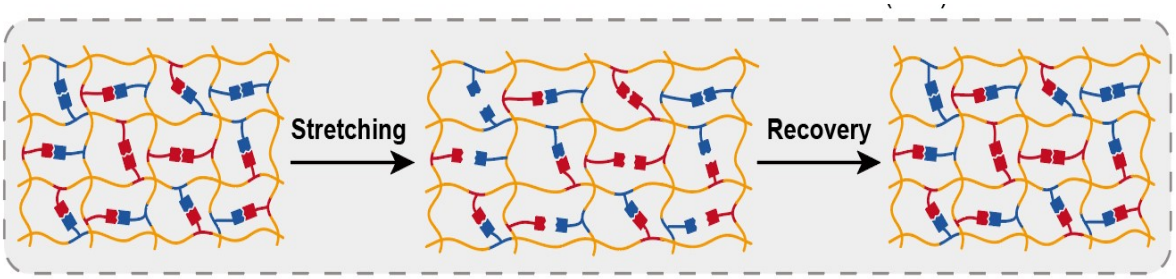

Figure S17. Schematic diagram of hydrogen bond dissociation and reconfiguration during loading-unloading of elastomers in a double-crosslinked network.

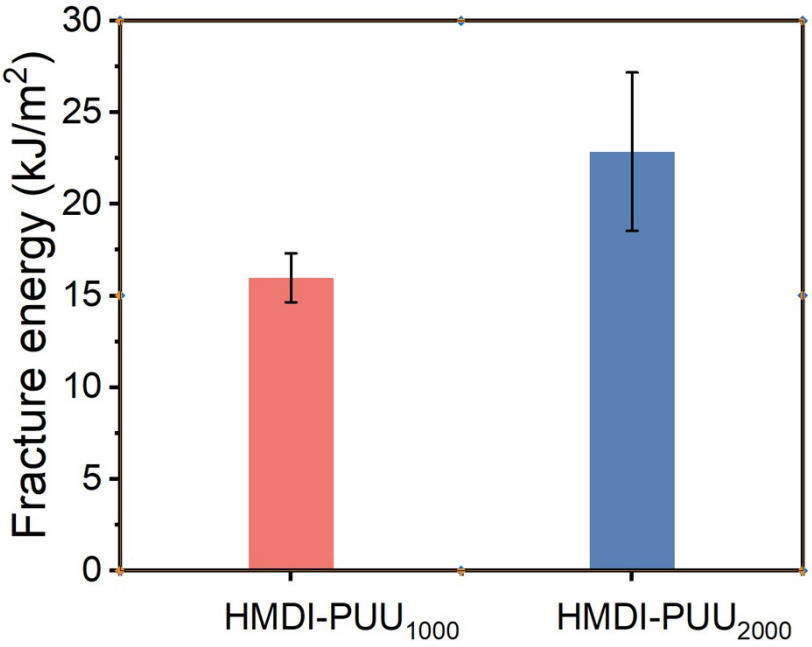

Figure S18. Fracture energies of the HMDI-PUU$_{1000}$ and HMDI-PUU$_{2000}$ samples.

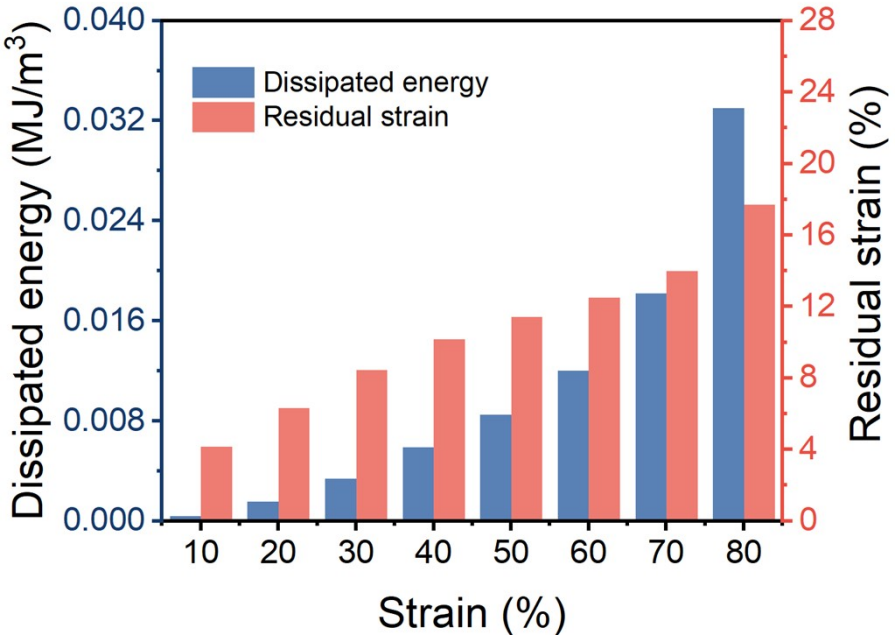

Figure S19. Calculated dissipation energy and residual strain for cycle numbers ranging from 1 to 100.

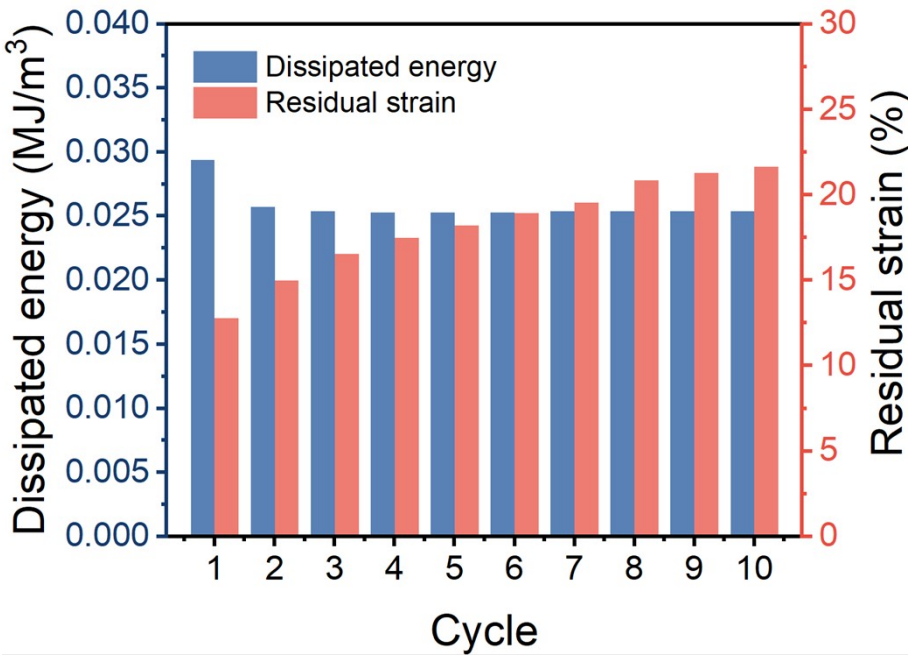

Figure S20. Calculated dissipation energy and residual strain for cycle numbers ranging from 1 to 10.

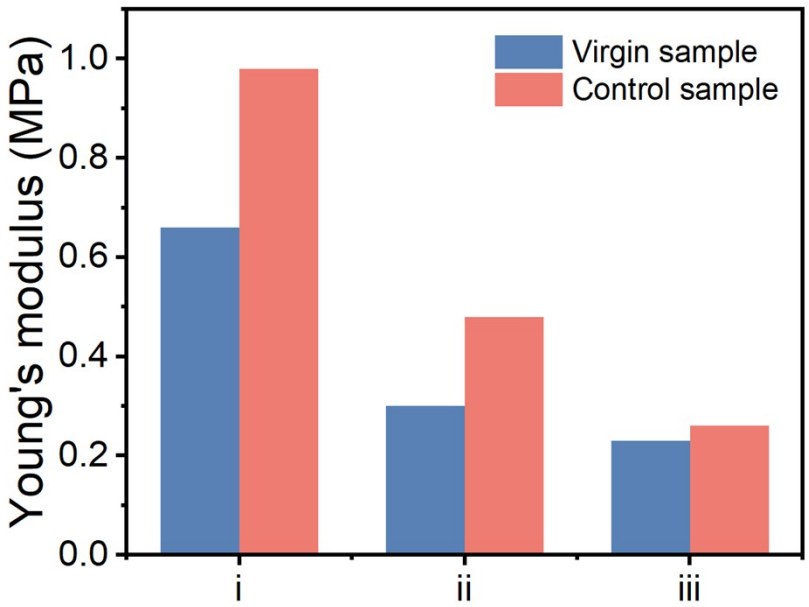

Figure S21. Compression modulus of stents of different sizes.

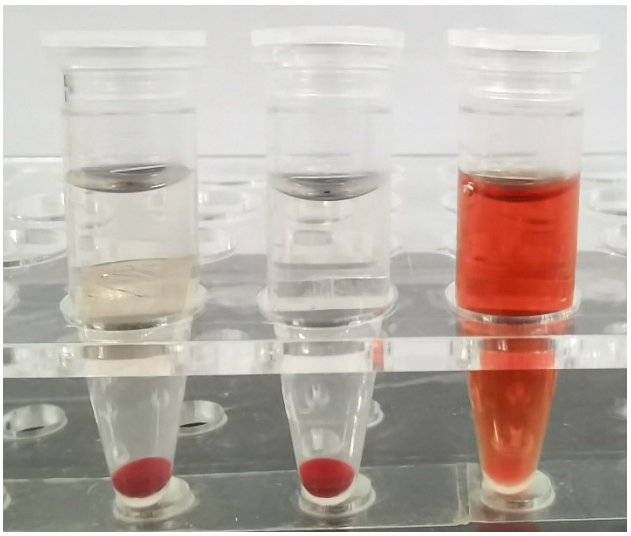

Figure S22. Relative erythrocyte hemolysis rate after centrifugation of centrifuge tube photographs.