

Lignocellulosic biomass-derived polyurethane elastomer with high toughness and excellent crack tolerance

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1. Experimental section

1.1. Materials

N,N-dimethylacetamide (DMAc), hexamethylene diisocyanate (HMDI), ethyl alcohol, glycerol, polyethylene glycol 400 (PEG-400), tetrahydrofuran (THF), and ditin butyl dilaurate were purchased from Aladdin Industrial Corporation. Concentrated sulfuric acid was obtained from Guangzhou Chemical Reagent Factory. Banana pseudo-stem from Haikou, China, was dried, milled and sieved to 50 meshes. PCL diol ($M_n = 2000$) was acquired from Guangdong Juyuan Plastic Auxiliary Chemical Co., Ltd. Polydimethylsiloxane (PDMS) was synthesized according to the literature.¹

1.2. Preparation

1.2.1. Preparation of the liquefied banana pseudo-stem mixture

The liquefaction process of LB was based on the previous studies.^{2,3} Specifically, the banana pseudo-stem was pre-treated by ball milling to decrease its size and molecular weight. Subsequently, the pre-treated stem (30g), PEG 400 (120 g), glycerin (30 g), and sulfuric acid (10.29 g) were added to a three-necked flask, and the obtained mixture was stirred at 140 °C for 120 min, followed by rapid cooling in an ice bath to quench the reaction. Next, the black mixture was diluted with ethanol, which was vacuum-filtrated through filter paper with a pore size of 11 μm. Finally, the liquefied LB was obtained by removing ethanol with a rotary evaporator. The hydroxyl number was determined and shown in the following section.

1.2.2. Preparation of the PUs

PCL diol (28 g) was first dissolved in a solvent mixture of THF (70 mL) and DMAc (50 mL) at 70 °C in a three-necked flask sealed with a rubber septum. HDMI (5.6 g) and ditin butyl dilaurate (0.1 g) were then added to the solution, and the resulting mixture was stirred and heated at 70 °C for 4.5 h to prepare the prepolymer solution. Subsequently, a DMAc solution of liquified LB (20 mL) was added to the prepolymer solution, in which the mass content of LB was 2, 3, 4, and 5% relative to PCL diol; the corresponding PU material was denoted as PU-X (X = 2, 3, 4 and 5). The resulting mixture was stirred continuously at room temperature (24 °C) for 24 h, casted on a glass plate, and then dried at 70 °C. The obtained film was immersed in ethanol to remove impurities and then dried at 70 °C to obtain the final PU elastomers.

1.3. Characterization

1.3.1. General characterization

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy (Nicolet iS10, Thermo Fisher Scientific, USA) was utilized to determine the chemical composition of the materials. Variable temperature infrared spectroscopy (VTIS, Thermo IS 50) was used to determine the changes in the hydrogen bonds. Solid-state ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 500 MHz spectrometer (Bruker, AVANCE III). Differential scanning calorimetry (DSC) measurements were conducted on a TA Discovery DSC 250 analyzer under a N₂ atmosphere with a heating rate of 10 °C min⁻¹. X-ray diffraction (XRD) patterns were obtained on Bruker D8 diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). A Bruker multimode series atomic force microscopy (AFM) system with a Nanoscope 8 controller in Peak Force Quantitative Nanomechanical Mapping (QNM) mode was used to measure the phase morphology and surface modulus. Small-angle X-ray scattering (SAXS) measurements were carried out on Bruker Nanostar SAXS spectrometer. The storage modulus, loss modulus and stress relaxation were determined by dynamic mechanical analysis (DMA, Q850, TA Instruments). The phase dispersion of PU matrix was observed by Talos F200X G2 transmission electron microscope

(TEM) with an accelerating voltage of 200 kV. The thin sections (~70 to 80 nm and dyed by tungsten phosphate) for TEM observations were cut by a microtome at -100 °C and collected on copper grids.

1.3.2 Mechanical tests

The mechanical properties of the prepared samples were analyzed using an electronic universal testing machine (Instron 68TM-5) at a rate of 30 mm min⁻¹. The samples for the uniaxial tensile tests were cut into dog-bone shape with a width of 4 mm and a length of 50 mm. During the test, the sample was glued to the gripper using foam tape (3M). The toughness of the sample was obtained by integrating the areas under the stress–strain curves. The fracture energy of the sample was obtained using a pure-shear test according to the following equation:^{4,5}

$$\Gamma = W(\lambda c)H,$$

where H is the distance between the two clamps under zero deformation, and $W(\lambda c)$ is the energy per volume of the uncut sample stretched at the critical strain λc for crack propagation. The energy density $W(\lambda c)$ was obtained by integrating the area below the

stress–strain curve of the uncut sample ($W(\lambda) = \int_0^{\lambda} s d\lambda$). The width and length of the rectangular sample between the two clamps were 25 and 5 mm, respectively, while the notch size of the sample was 10 mm.

For the determination of stress concentration factor and radius of curvature, a sample with ~20 mm in length between two clamps and ~60 mm in width was used. The crack was approximated as an ellipse and was considered to conform to the elliptic equation, that is $x^2/c^2 + y^2/b^2 = 1$ (see Figure 4e). Thus, the crack tip has the minimum radius of curvature ($p = b^2/c$), and the maximum stress concentration can be found at the crack tip (Point-B), valuing at $\sigma_B = \sigma_A(\text{applied external stress}) \times (1+2c/b)$. Ultimately, the stress concentration factor is equal to σ_B/σ_A .

1.3.3. Recycling test and cytocompatibility study

The recycling test was conducted by hot-pressing the PU-3 fragments at 140 °C and 15 MPa for ~1 h by a molding machine (QLB-D, Shanghai Rubber Machinery NO.1 Factory).

For the bio test, the cell used in the experiment was mouse fibroblast cell (L929), and the cell medium was RPMI-1640 complete medium containing 10% fetal bovine serum (FBS, BI, Israel). Detailed bio experimental section can be obtained from previously reported work.⁶

1.3.4. Determination of hydroxyl number of liquified LB⁷

A mixture of 1 g liquefied material with 25 mL phthaloylated solution (116 g phthalic anhydride, 16 g imidazole and 700 mL pyridine) was heated at 110°C for 20 min. 50 mL 1, 4-dioxane and 25 mL distilled water were then added, and the mixture was titrated with a 1 mol L⁻¹ NaOH solution to a pH of 7. Hydroxyl number (mg KOH/g) was calculated using the equation:

$$\text{Hydroxyl number} = \frac{(B - A) \times 56.1}{W} + \text{Acid number}$$

where A is the volume of NaOH solution needed to titrate the sample, B is volume of NaOH solution consumed for blank titration, W is the mass of liquified LB mixture, and 56.1 is molar mass of potassium hydroxide.

As for the determination of acid number of liquified LB mixture, 5 g liquified LB mixture was dissolved in 100 mL 1, 4-dioxane-water solution (volume ratio was 4:1), and the above mixture was titrated with 1 mol L⁻¹ NaOH solution to neutral. The acid number of the liquefied material (mg KOH/g) was calculated by the formula:

$$\text{Acid number} = \frac{(C - D) \times N \times 56.1}{W}$$

where C is the volume of NaOH solution needed to titrate the sample, D is volume of NaOH solution consumed for blank titration, W is the mass of liquified LB mixture, N is the concentration of NaOH solution, and 56.1 is molar mass of potassium hydroxide.

Ultimately, the obtained hydroxyl number was 241.6 ± 13.7 mg KOH/g.

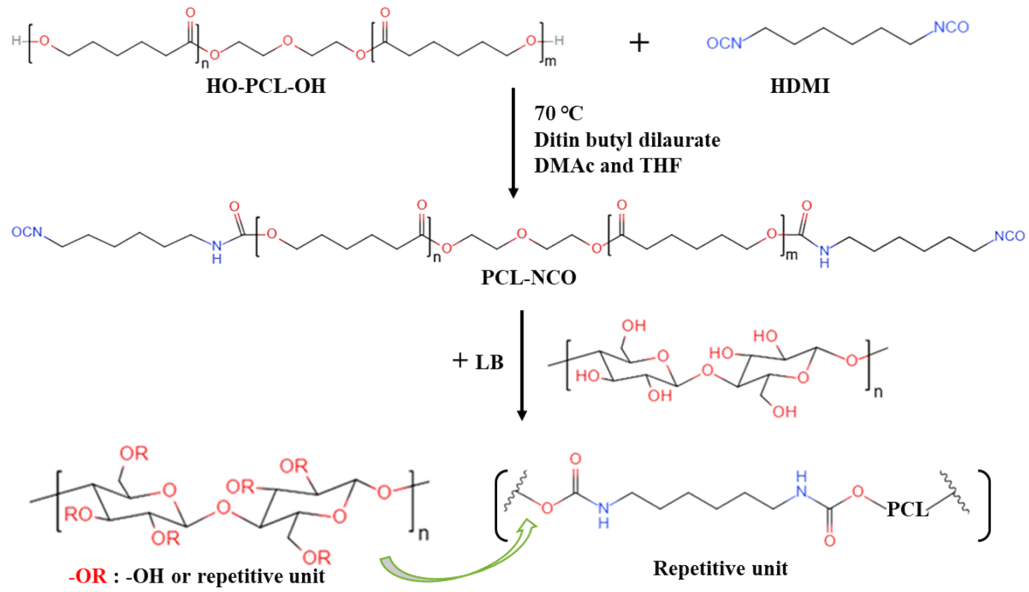


Figure S1. Schematic of synthetic routes for PU elastomers (cellulose, one of the main components of liquified LB, was used to represent the structure of the chain extender).

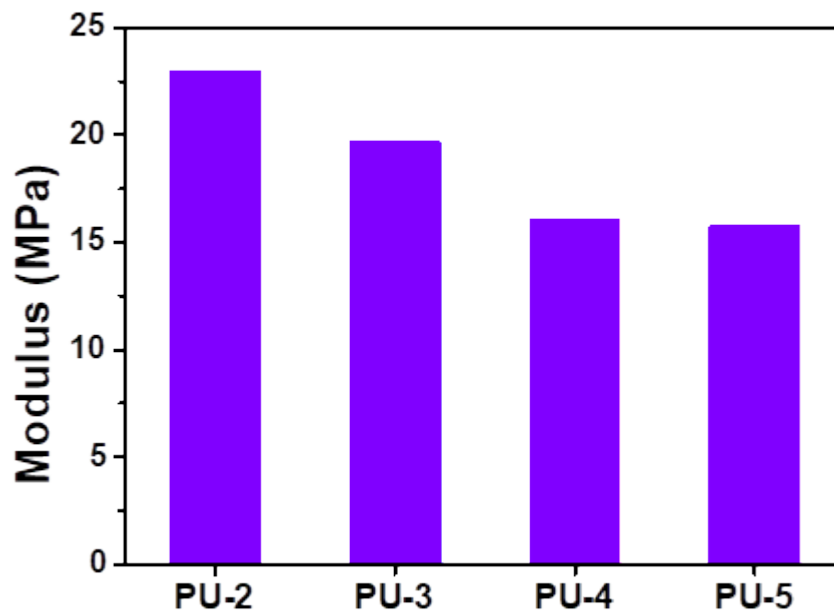


Figure S2. Modulus of various samples obtained from tensile curves.

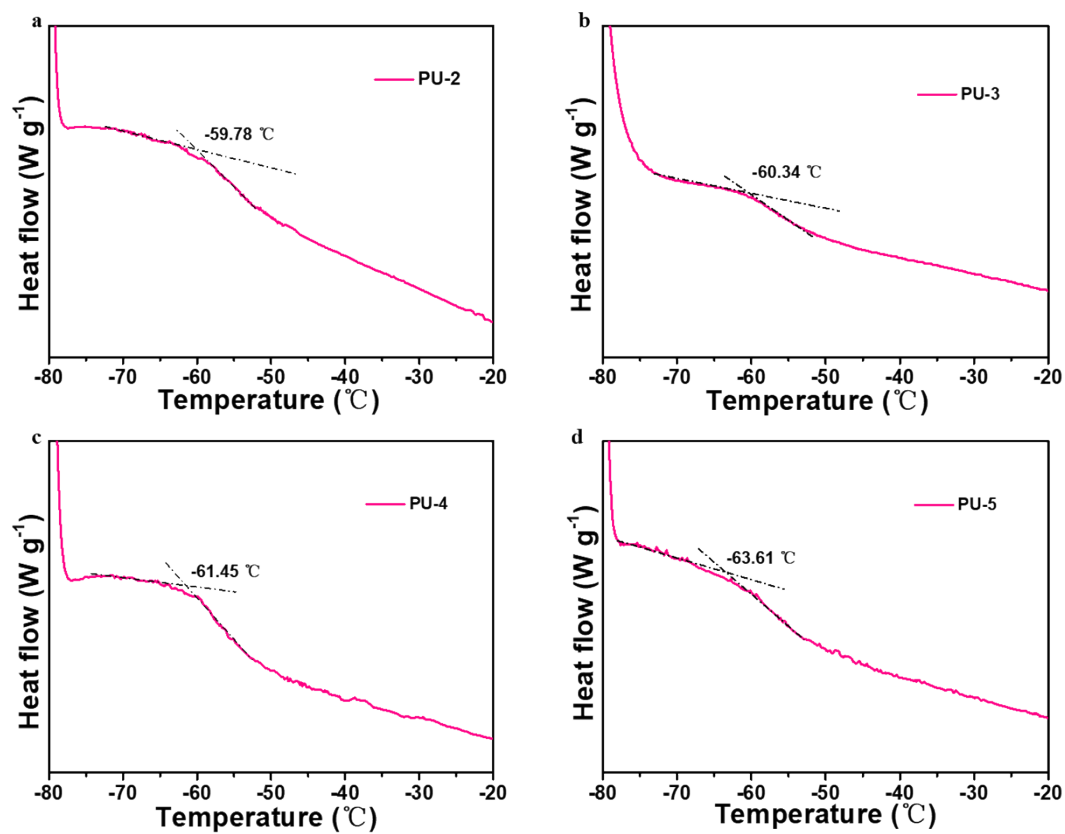


Figure S3. DSC curves and T_g of various samples.

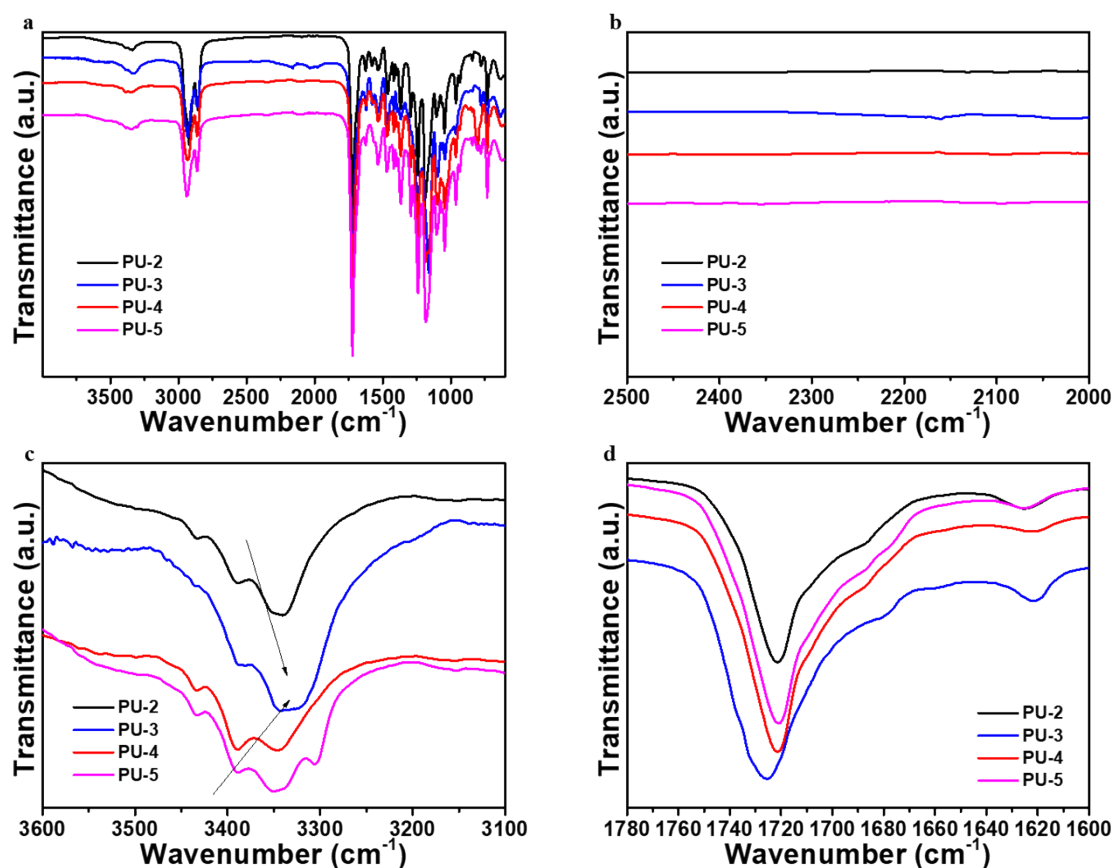


Figure S4. FTIR spectra of various samples, and their partial enlarged views.

Table S1. The assignment of the deconvoluted subpeaks in the FTIR C=O absorption bands of PU-3.

Assignment		Wavenumber (cm ⁻¹)
ν (C=O) urethane amide	Free	2 (1732), 3 (1724)
	H-bonded (Ordered)	1 (1737), 4 (1712)
ν (C=O) urea amide	Free	5 (1680)
ν (C=O) amide	H-bonded (Ordered)	6 (1621), 7 (1618)

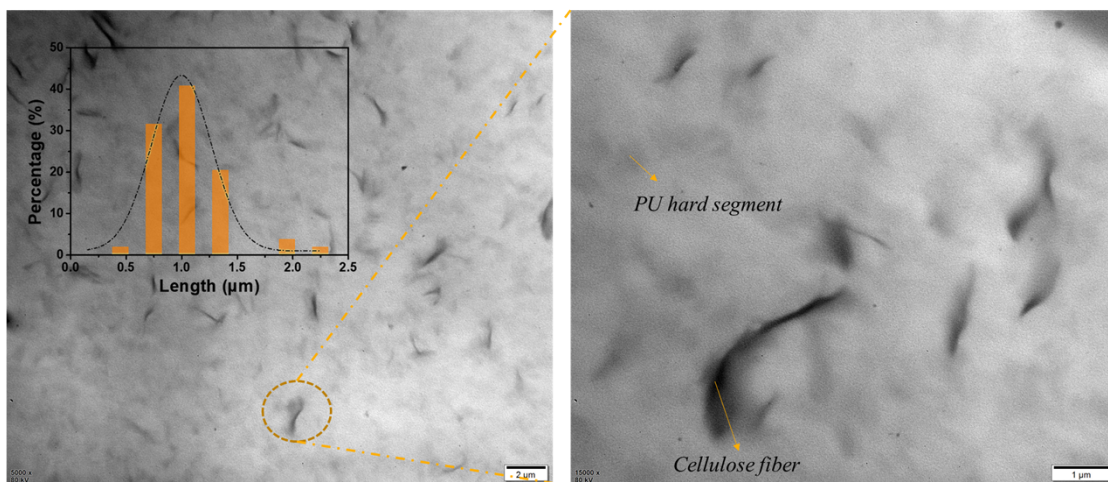


Figure S5. TEM images of PU matrix. Insert: size distribution of the cellulose fibers in the PU matrix.

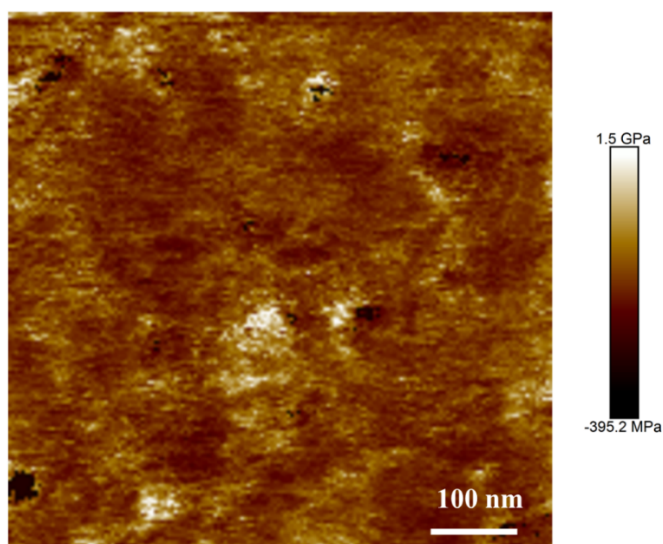


Figure S6. AFM modulus image of PU-3.

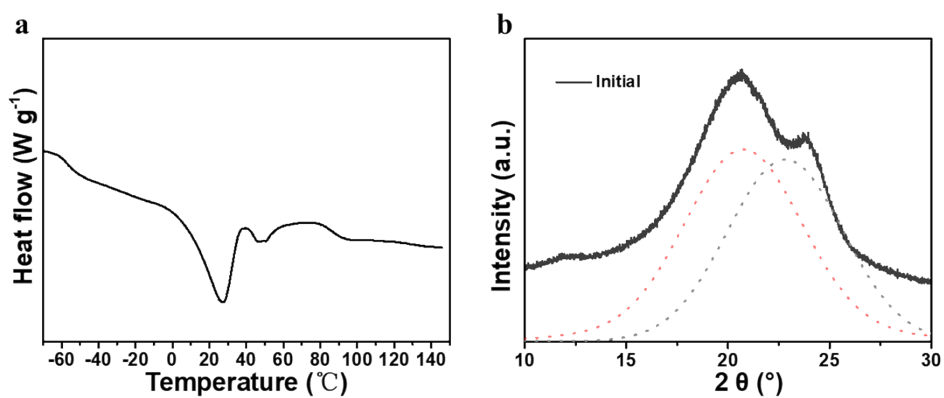


Figure S7. (a) DSC curve of PU-3, in which the peaks at ~30 and ~50 °C belong to PCL crystal and lignin, respectively,^{6, 8} and (b) XRD result and split peaks of PU-3 at

initial condition.

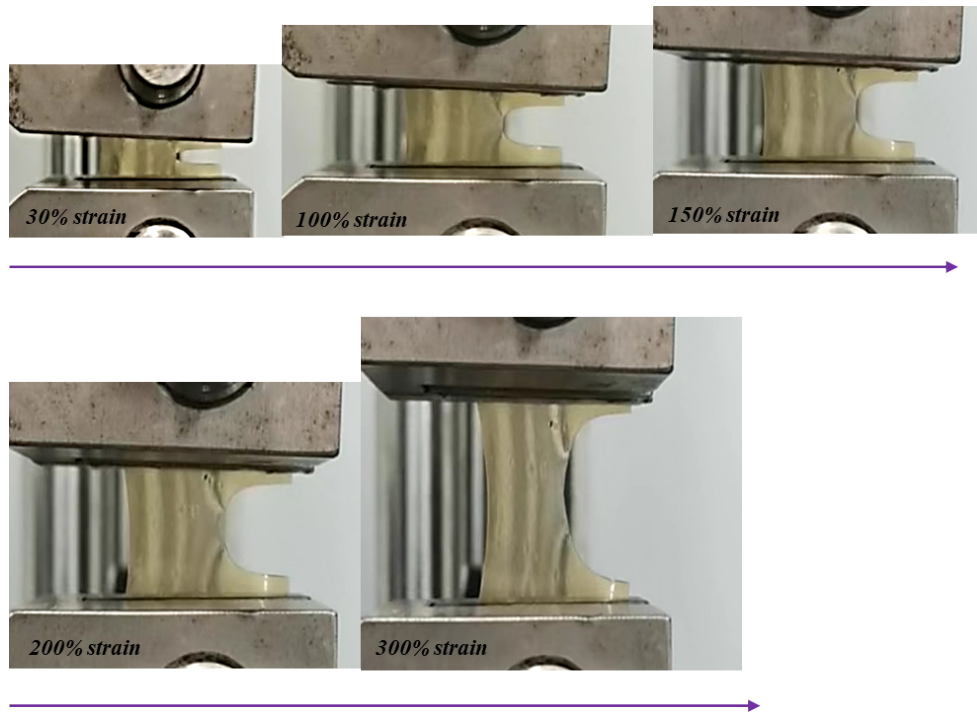


Figure S8. Notched PU-3 elastomer at different strains.

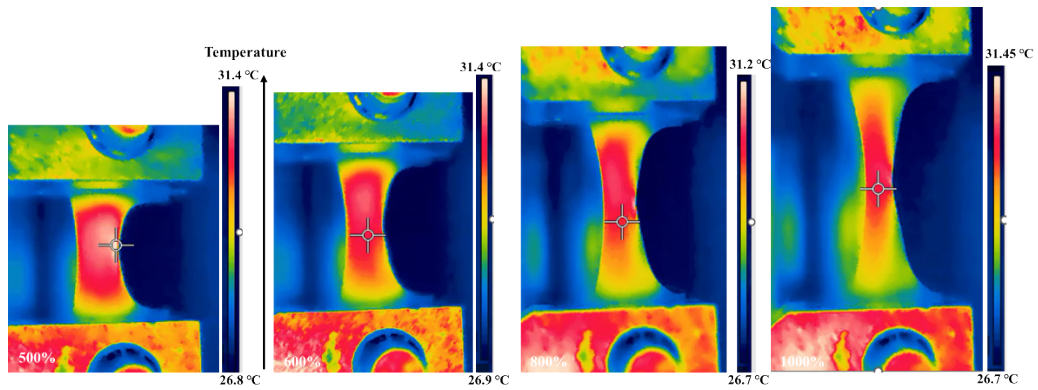


Figure S9. Infrared images of 10 mm-notched PU-3 elastomer at different strains.

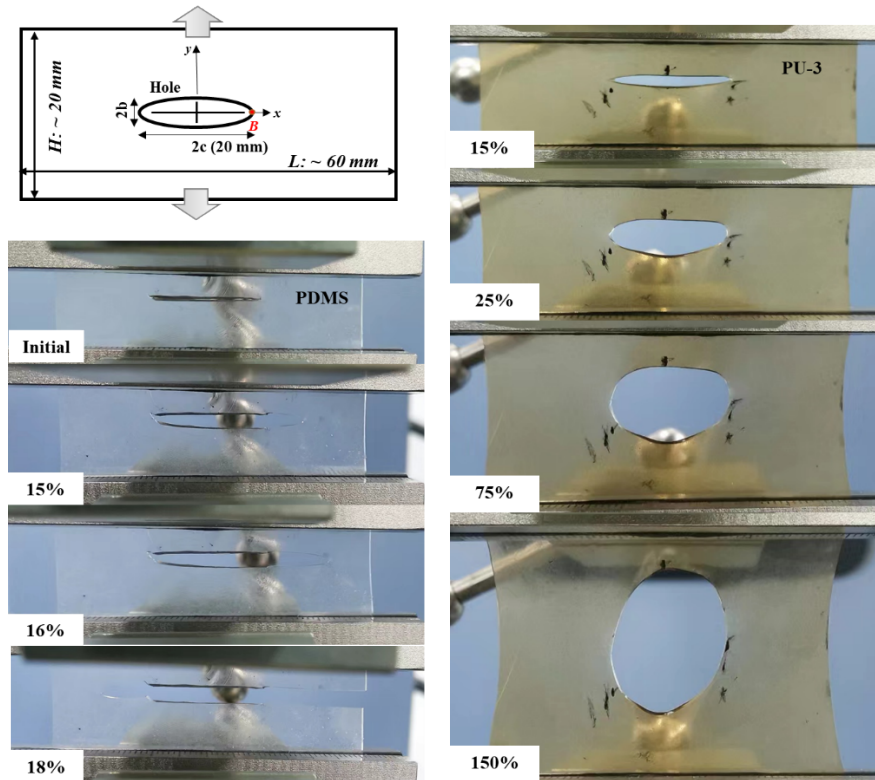


Figure S10. Crack growth behavior of PDMS and PU-3 elastomers with $\sim 20 \text{ mm}$ initial crack at different strains.

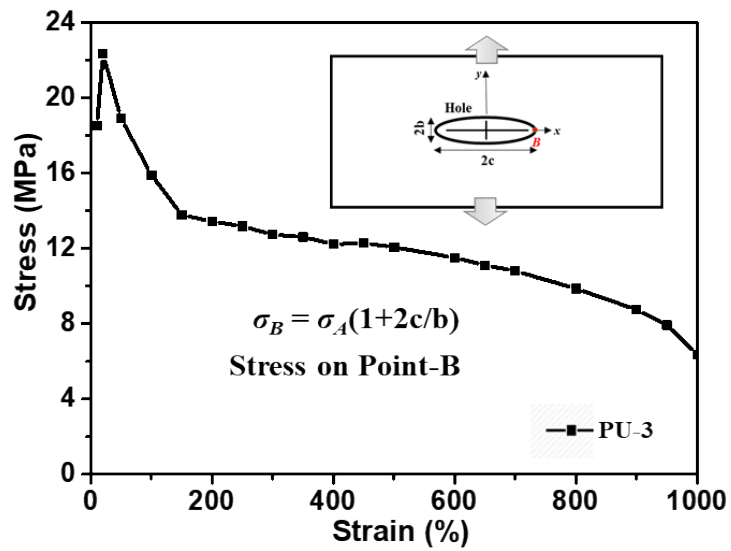


Figure S11. Stress at crack tip-B.

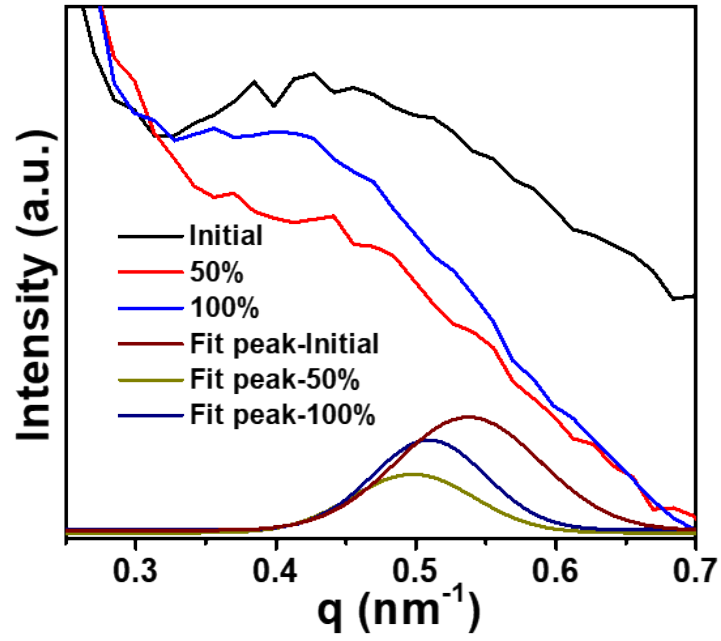


Figure S12. Split shoulder peaks of PU-3 at different strains.

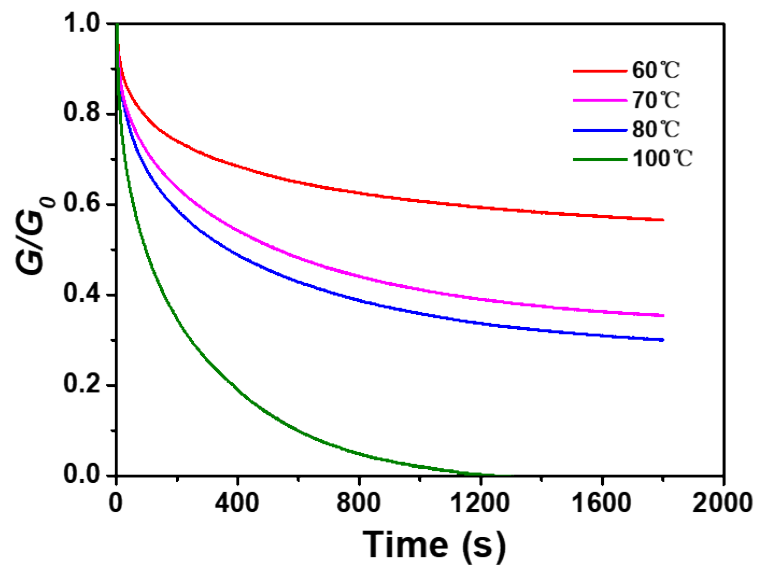


Figure S13. The stress-relaxation curves of PU-3 from 60 to 100 °C

Reference

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