

Supplementary Information

Sunlight driven self-healing, reshaping and recycling of robust, transparent and yellowing-resistant polymer

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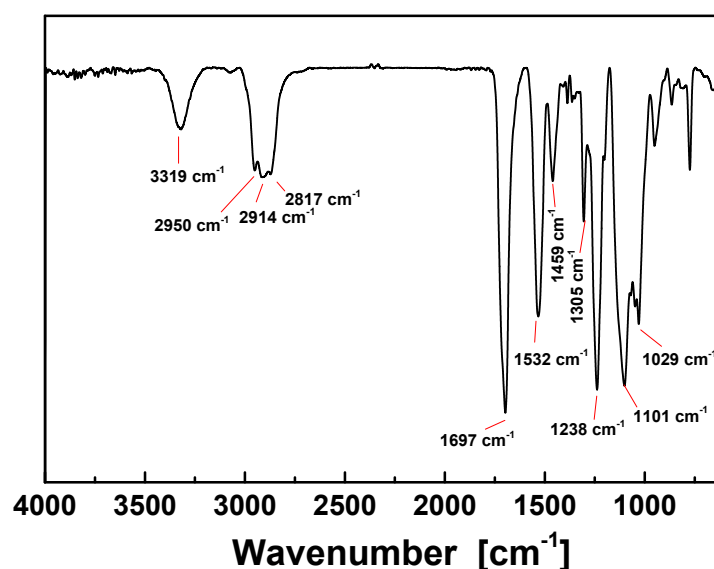


Figure S1. FTIR spectrum of PU-HEDS-400 with the following characteristic peaks demonstrating its chemical structure: 3319 cm⁻¹ (ν (-NH-)), 2950, 2913 and 2871 cm⁻¹ (ν (CH₃,CH₂)), 1697 cm⁻¹ (ν_{as} (C=O)), 1532 cm⁻¹ (δ (C-N-H)), 1459 cm⁻¹ (δ (CH₂)), 1305 cm⁻¹ (δ (C(C=O)-N-H)), 1238 and 1101 cm⁻¹ (ν (C-O-C)), 1048 and 1029 cm⁻¹ (δ (C-O-C)).

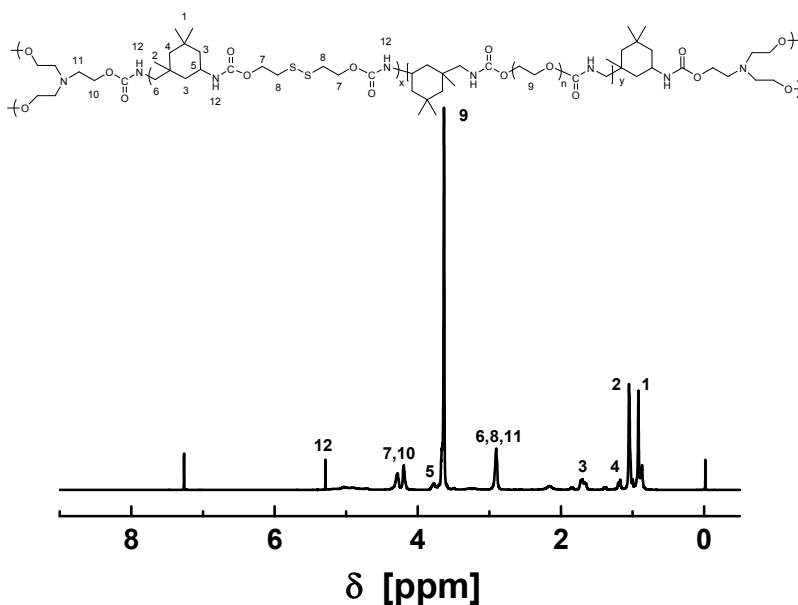


Figure S2. ¹H NMR spectrum (CDCl₃) of PU-HEDS-400. δ (ppm) = 7.27 (CDCl₃), 5.29 (12H, -NH), 4.29-4.19 (7H, 10H, -O-CH₂-), 3.77 (5H, C-H), 3.63 (9H, -CH₂-CH₂- of PEG400), 2.90 (6H, 8H, 11H, -N-CH₂-, S-CH₂-), 1.72-1.67 (3H, -CH₂- of IPDI), 1.20-1.17 (4H, -CH₂- of IPDI), 1.050 (2H, -CH₃ of IPDI), and 0.92 (1H, -CH₃ of IPDI).

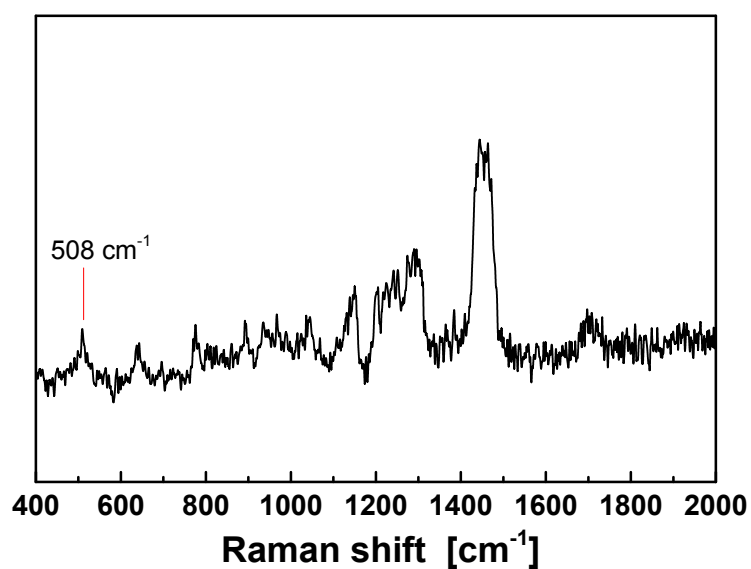


Figure S3. Raman spectrum of PU-HEDS-400. The peak at 508 cm⁻¹ is attributed to S-S bond.

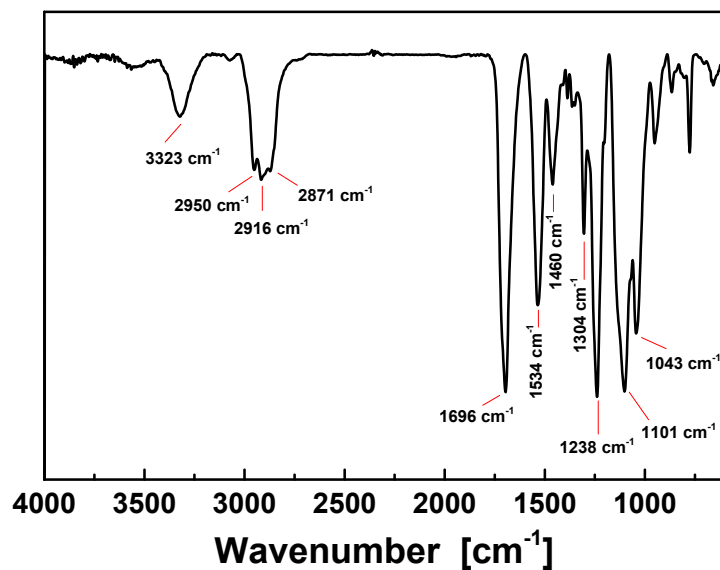


Figure S4. FTIR spectrum of PU-BDO-400 with the following characteristic peaks demonstrating its chemical structure: 3323 cm^{-1} ($\nu(-\text{NH}-)$), 2950, 2916, 2871 cm^{-1} ($\nu(\text{CH}_3, \text{CH}_2)$), 1696 cm^{-1} ($\nu_{\text{as}}(\text{C}=\text{O})$), 1534 cm^{-1} ($\delta(\text{C}-\text{N}-\text{H})$), 1460 cm^{-1} ($\delta(\text{CH}_2)$), 1304 cm^{-1} ($\delta(\text{C}(\text{C}=\text{O})-\text{N}-\text{H})$), 1238 and 1101 cm^{-1} ($\nu(\text{C}-\text{O}-\text{C})$), 1043 cm^{-1} ($\delta(\text{C}-\text{O}-\text{C})$).

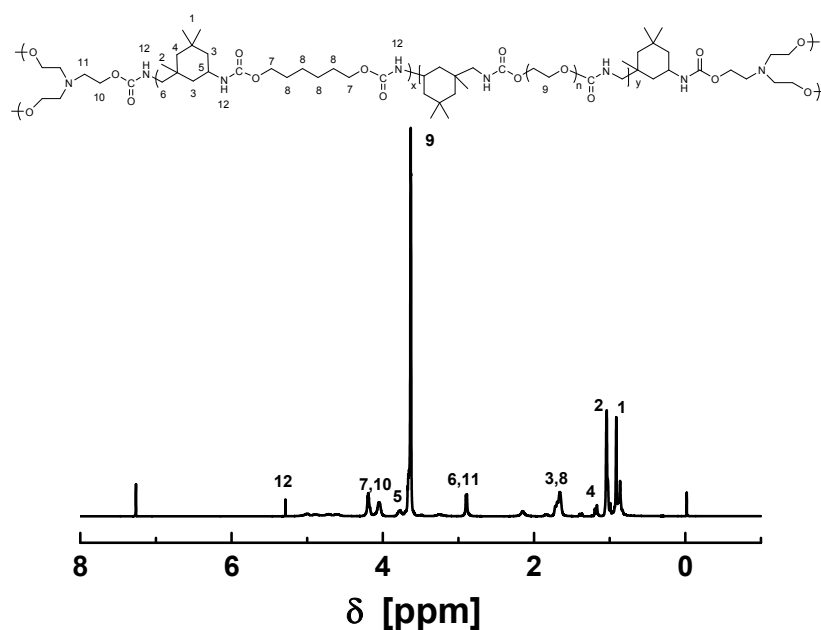


Figure S5. ^1H NMR spectrum (CDCl_3) of PU-BDO-400. δ (ppm) = 7.26 (CDCl_3), 5.29 (12H, $-\text{NH}$), 4.20-4.04 (7H, 10H, $-\text{O}-\text{CH}_2-$), 3.77 (5H, C-H), 3.63 (9H, $-\text{CH}_2-\text{CH}_2-$ of PEG400), 2.89 (6H, 8H, 11H, $-\text{N}-\text{CH}_2-$, S- CH_2-), 1.66 (3H, 8H, $-\text{CH}_2-$), 1.19 (4H, $-\text{CH}_2-$ of IPDI), 1.04 (2H, $-\text{CH}_3$ of IPDI), 0.91 (1H, $-\text{CH}_3$ of IPDI).

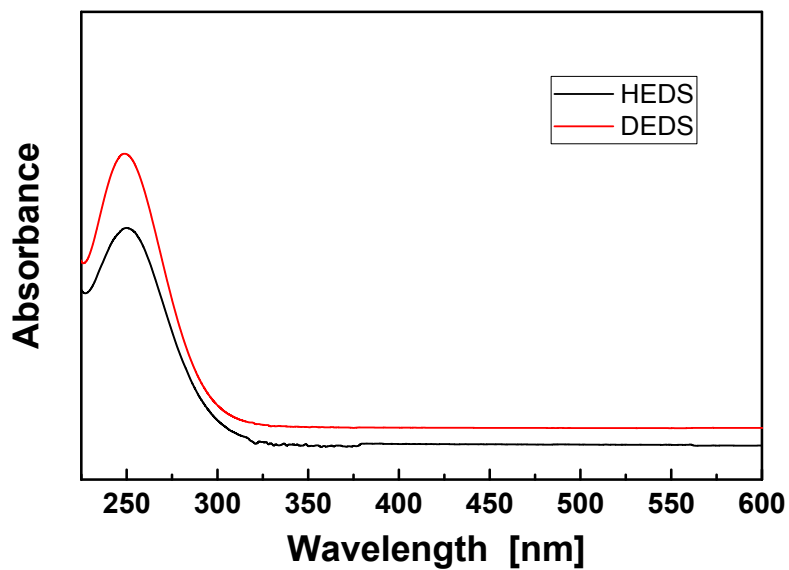


Figure S6. UV-visible spectra of DEDS and HEDS in acetonitrile (0.01mmol/ml).

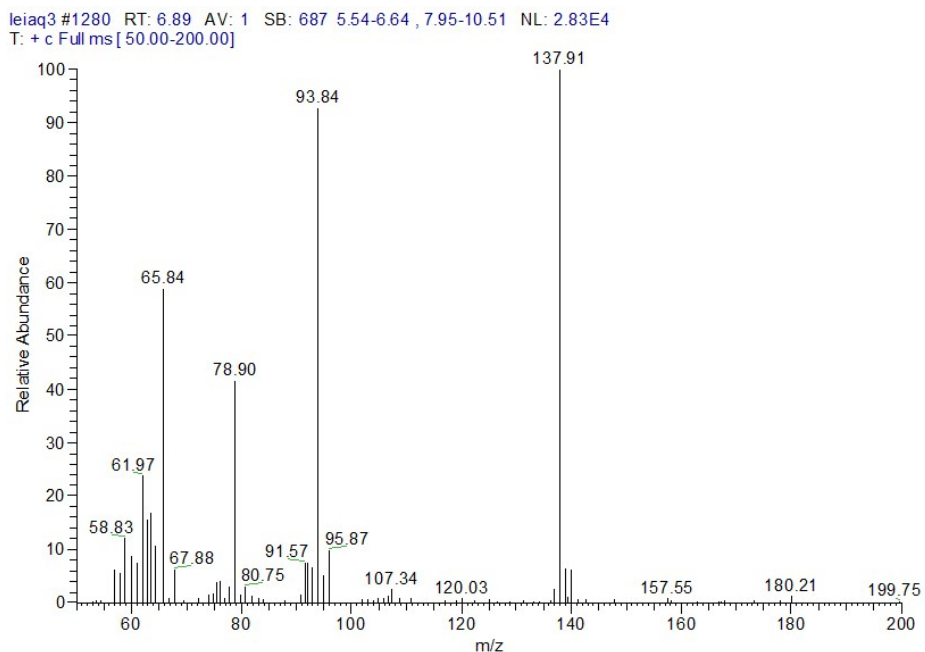


Figure S7. Mass spectrum of the product of exchange reaction between DEDS and HEDS, i.e. ethyl propyl disulfide (HEED).

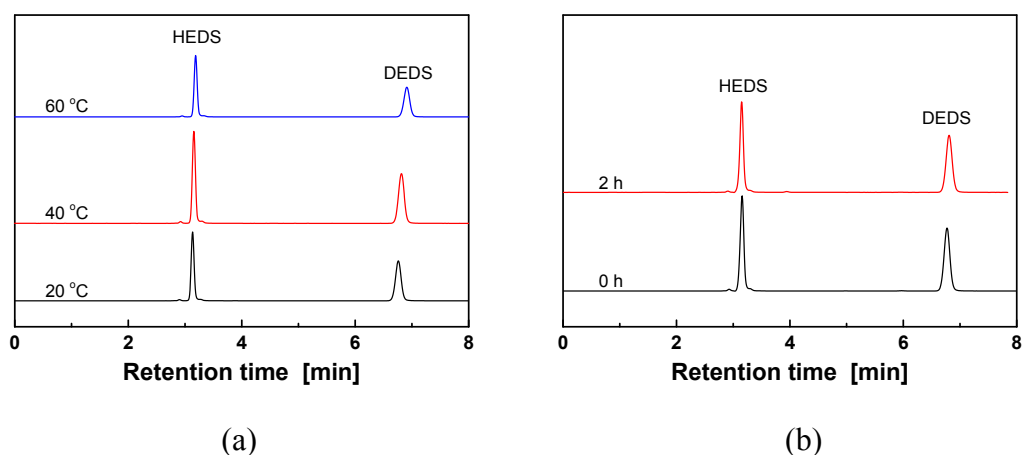


Figure S8. (a) HPLC analysis of an equimolar mixture of DEDS and HEDS in acetonitrile heated at different temperatures for 2 h in the dark. (b) HPLC analysis of an equimolar mixture of DEDS and HEDS in acetonitrile exposed to visible light with intensity of 90 mW/cm^2 (which is yielded by filtering out UV rays from xenon lamp light).

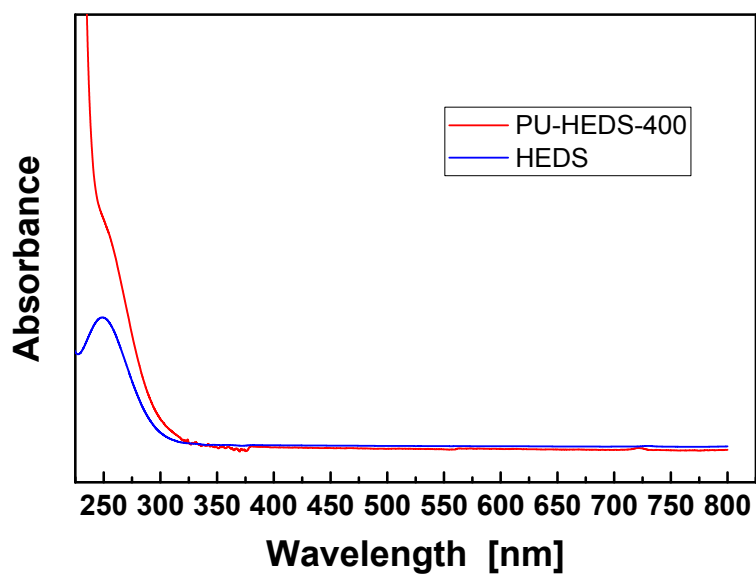


Figure S9. UV-visible spectra of prepolymer PU-HEDS-400 in dichloromethane (5 mg/ml) and HEDS in acetonitrile (0.01 mmol/ml).

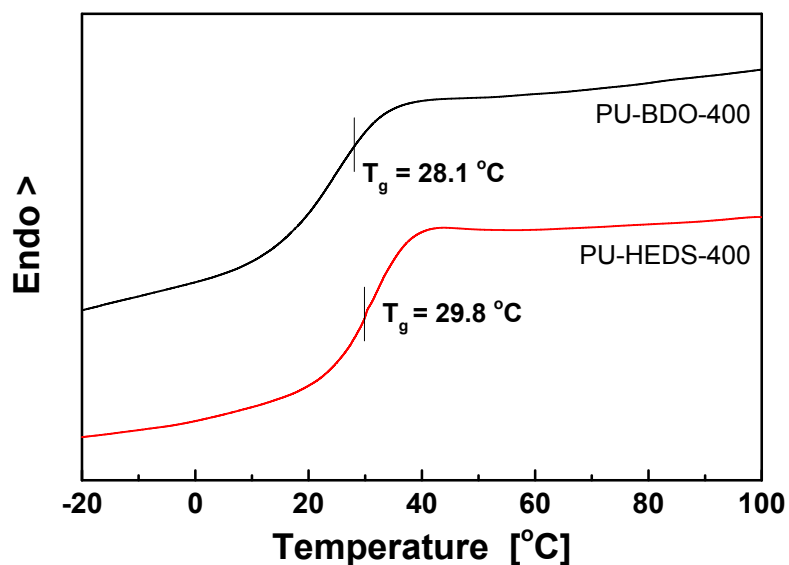


Figure S10. DSC heating curves of PU-HEDS-400 and PU-BDO-400.

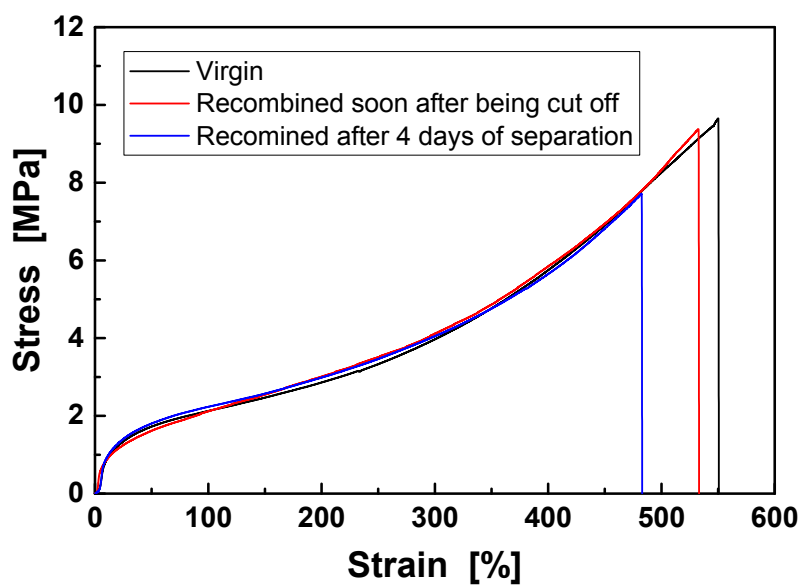


Figure S11. Tensile stress-strain curves of virgin and healed PU-HEDS-400 specimens. Healing was conducted under xenon lamp light (intensity = 100 mW cm^{-2}) for 24 h. The healing efficiencies are estimated to be 79.9 and 97.1 % for the specimens that are recombined (i) after 4 days of separation and (ii) immediately after being cut off, respectively.

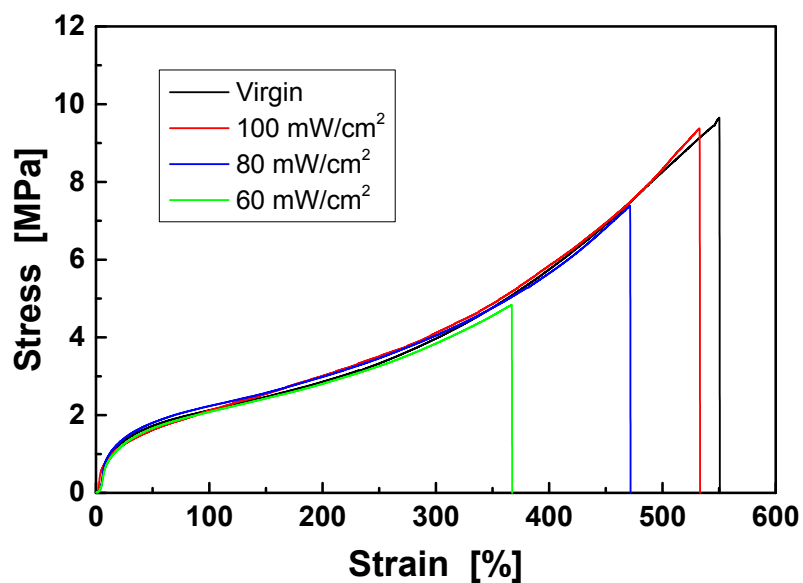


Figure S12. Tensile stress-strain curves of virgin and healed PU-HEDS-400 specimens. Healing is conducted under xenon lamp light with different intensities for 24 h. The healing efficiencies are estimated to be 50.1, 76.5, and 97.1 % for 60, 80 and 100 mW cm⁻², respectively.

Table S1. Mechanical properties and healing efficiencies of PU-HEDS-400 and its control PU-BDO-400

Polymers	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Healing efficiency* (%)
PU-HEDS-400	5.04±0.05	9.67±0.89	553±7.64	95.4±0.9
PU-BDO-400	5.12±0.03	9.85±1.24	531±2.92	41.6±2.3

*Healing is conducted under the illumination of xenon lamp light (intensity = 100 mW cm⁻²) for 24 h.

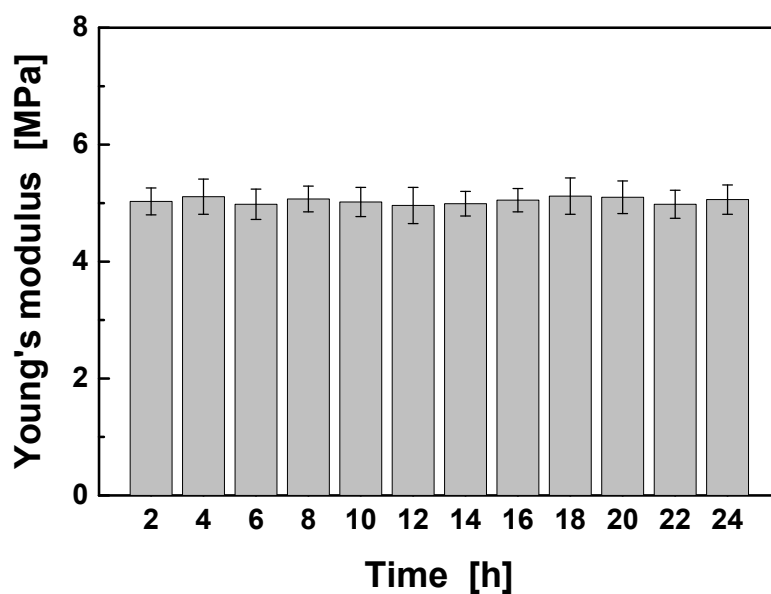


Figure S13. Time dependence of Young's modulus of PU-HEDS-400 specimens exposed to xenon lamp light (intensity = 100 mW cm⁻²).

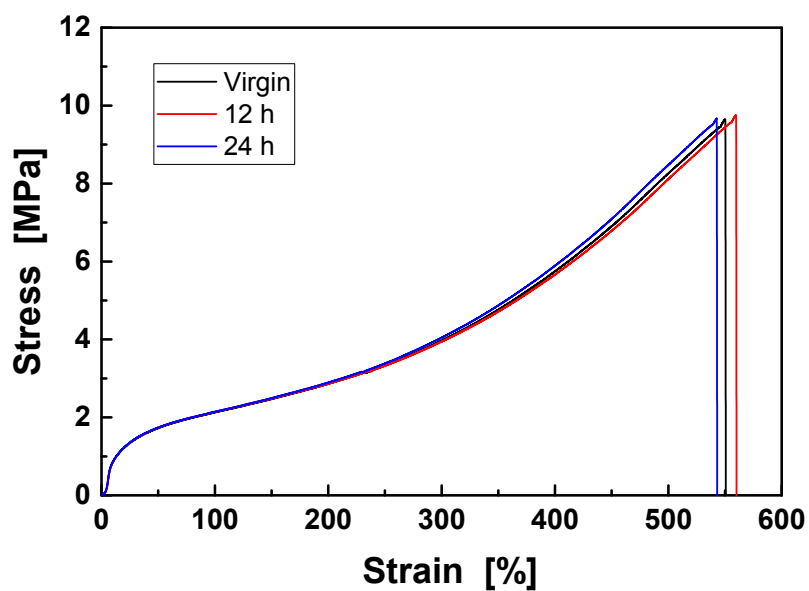


Figure S14. Typical tensile stress-strain curves of PU-HEDS-400 specimens exposed to xenon lamp light (intensity = 100 mW cm⁻²) for different times.

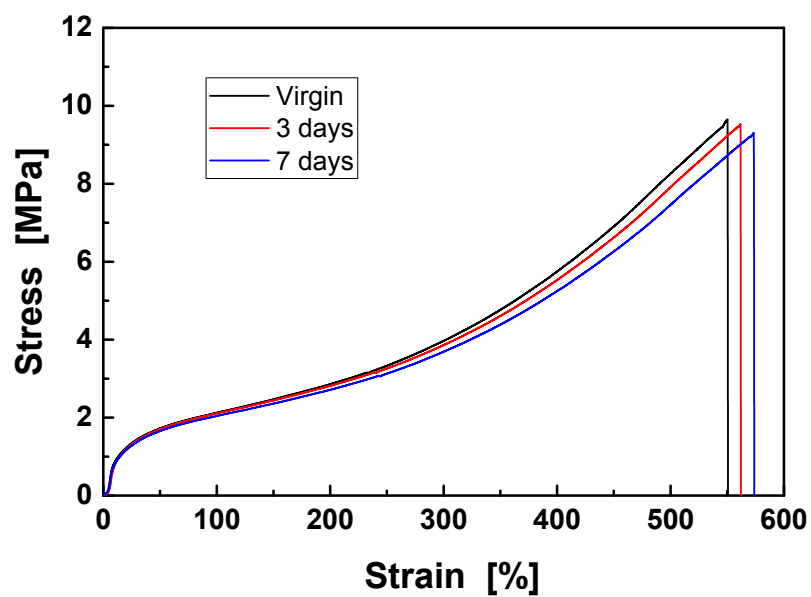


Figure S15. Typical tensile stress-strain curves of PU-HEDS-400 specimens exposed to sunlight from 10:00 am to 4:00 pm in July for different times.