Electronic Supplementary Information (ESI)

Eugenol-based polyester and its bamboo fiber composite with enhanced mechanical and anti-ultraviolet properties

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I. Experimental Section

Characterization

^{1}H (500 MHz) and ^{13}C (126 MHz) NMR spectra were recorded on a Bruker 500 MHz spectrometer using tetramethylsilane as an internal standard. FT-IR spectra of polymers were recorded using attenuated total reflectance (ATR) measurements in the range of 4000-400 cm^{-1} on a Thermo Nicolet 380. Gel permeation chromatography (GPC) was used to evaluate the relative molecular weight (M_n) and dispersity ($Đ$) of polymers, which equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (7.8 × 300 mm, 5 mm bead size; 10^3, 10^4, and 10^5 Å pore size). The measurements were conducted at 35 °C using polystyrene standard to calibrate the system, and using THF as the eluent with a flow rate of 1.0 mL min^{-1}. The glass transition temperature (T_g) was measured by a Q2000 DSC device at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. All the samples were first heated from -70 °C to 160 °C and held at this temperature for 3 min to eliminate the thermal history, and then they were cooled to -70 °C and heated again from -70 to 160 °C at a heating or cooling rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) of polymers was conducted with an SDT851e/SF/1100, under nitrogen flow at a heating rate of 10 °C min^{-1} from 25 °C to 800 °C. Tensile tests were conducted on HY-0580 electronic tensile tester (Shanghai Hengyi Testing Instruments Co., Ltd.) and transcell load cell used (BSS-500 kg). The dumbbell-shaped samples with an effective gauge length of 12 mm, a width of 2 mm, and a thickness of 1 mm were prepared by using a hand operated cutting press. The stress-strain curves were obtained by deformation rate of 50 mm min^{-1} at room temperature. The surface characteristic of polymer composite film was observed by optical microscope Axio scope A1.

The sol fraction and crosslinking density were calculated by an equilibrium swelling experiment. The specific experimental steps are as follows: weigh the sample with an initial mass (m_0), then soak the sample in toluene for 72 h, and replace with a new solvent every 24 h. After swelling equilibrium, wipe the solvent on the sample surface with filter paper quickly, and weigh the mass (m_1) of the sample after swelling immediately. Finally, dry it in a vacuum at 60 °C to constant weight (m_2). Three specimens were measured for each sample, and the average value and standard deviation were calculated.

$$\text{sol fraction} = \frac{m_0 - m_2}{m_0} \quad (1)$$

$$\text{crosslinking density: } V_e = \frac{\ln(1 - V_r) + V_r + \chi {V_r}^2}{V_s\left({V_r}^{1/3} - V_r/2\right)} \quad (2)$$

where χ is the Flory-Huggins polymer-solvent interaction parameter (0.44 for polyester/ toluene), and V_s is the molar volume of the solvent (toluene is 106.5 cm^3 mol^{-1}). V_r is the volume fraction of swelling polyester and can be calculated as follows:

$$V_r = \frac{\frac{m_2}{\rho_r}}{\frac{m_2}{\rho_r} + \frac{(m_1 - m_2)}{\rho_s}} \quad (3)$$

where ρ_r and ρ_s are the densities of polyester and toluene, respectively.

UV light transmittance curves were recorded on a UV2400 spectrometer (Shanghai Sunny Hengping Scientific Instrument Co., Ltd). The UV protection factor (UPF; eq 4) and average transmittance values of UVA light [T_{UVA}; eq 5] and UVB light [T_{UVB}; eq 6] were calculated as follows, according to profiles of UV Standard 801:

$$\text{UPF} = \sum_{290}^{400} E_\lambda S_\lambda / \sum_{290}^{400} E_\lambda S_\lambda T_\lambda \quad (4)$$

$$T_{UVA} = \frac{1}{m} \sum_{315}^{400} T_\lambda \quad (5)$$

$$T_{UVB} = \frac{1}{n}\sum_{290}^{315} T_{\lambda} \qquad (6)$$

Synthesis of monomers

Synthesis of eugenol acrylate (UGA)

A 250 mL three-neck flask was charged with UG (8.85 g, 60 mmol), acrylic acid (8.64 g, 120 mmol), DMAP (3.66 g, 30 mmol), and dry DCM (60 mL) under a nitrogen atmosphere. The mixture was stirring at ice-water bath for 15 min, then added EDCI·HCl (22.92 g, 120 mmol), and stirred at room temperature for 72 hours. It washed with distilled water (3×40 mL) and saturated NaCl aqueous solution (3×20 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The liquid was purified by column chromatography on silica gel using PE/EA (40:1) as eluent to afford colorless liquid **UGA** (8.53 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.02-7.01 (d, 2H, phenyl), 6.83-6.79 (t, 1H, phenyl), 6.64-6.60 (d, 1H, C*H*$_2$=CHCOO), 6.39-6.34 (m, 1H, CH$_2$=C*H*COO), 6.03-5.93 (m, 2H, C*H*$_2$=CHCOO and CH$_2$=C*H*CH$_2$), 5.13-5.10 (m, 2H, C*H*$_2$=CHCH$_2$), 3.81 (s, 3H, C*H*$_3$O), 3.41-3.40 (d, 2H, C*H*$_2$CH=CH$_2$); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 164.4, 151.1, 139.2, 138.1, 137.2, 132.5, 127.7, 122.8, 120.8, 116.1, 112.8, 55.9, and 40.3. MS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{13}H_{14}O_3$ 241.0840, found: 241.0839. ATR-IR (cm^{-1}): 2840 ($\nu_{Ar\text{-}OCH_3}$), 1750 ($\nu_{C=O}$), 1640 ($\nu_{Ph\text{-}H}$), 1450 ($\nu_{C=CH_2}$), 900-690 ($\nu_{Ar\text{-}H}$).

Synthesis of 1,4-eugenol succinate (UGS)

A 250 mL three-neck flask was charged with UG (19.70 g, 120 mmol), succinic acid (5.92 g, 50 mmol), DMAP (3.05 g, 25 mmol), and dry DCM (50 mL) under a nitrogen atmosphere. The mixture was stirring at ice-water bath for 15 min, then added EDCI·HCl (22.92 g, 120 mmol), and stirred at room temperature for 72 hours. It washed with distilled water (3×30 mL) and saturated NaCl aqueous solution (3×20 mL), and the organic layer was dried with

Na_2SO_4, filtered, and concentrated under reduced pressure. The liquid was purified by column chromatography on silica gel using PE/EA (30:1) as eluent to afford white solid **UGS** (14.47 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.97-6.96 (m, 2H, phenyl), 6.79-6.75 (m, 4H, phenyl), 6.00-5.92 (m, 2H, CH_2CH=CH_2), 5.13-5.09 (m, 4H, CH_2CH=CH_2), 3.80 (s, 6H, CH_3O), 3.39-3.37 (d, 4H, CH_2CH=CH_2), 3.04 (s, 4H, CH_2COO); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 170.5, 150.8, 139.2, 138.0, 137.1, 122.7, 120.7, 116.4, 112.9, 56.0, 40.1, and 29.2. MS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{24}H_{26}O_6$ 433.1729, found: 433.1633. ATR-IR (cm^{-1}): 2840 ($\nu_{O\text{-}CH_3}$), 1750 ($\nu_{C=O}$), 1640 ($\nu_{Ph\text{-}H}$), 1450 ($\nu_{C=CH_2}$), 900-690 ($\nu_{Ar\text{-}H}$).

Synthesis of 2,5-eugenol furandicarboxylate (UGF)

A 250 mL three-neck flask was charged with UG (29.52 g, 180 mmol), FDCA (9.36 g, 60 mmol), DMAP (3.05 g, 25 mmol), and dry DCM (60 mL) under a nitrogen atmosphere. The mixture was stirring at ice-water bath for 15 min, then added EDCI·HCl (27.90 g, 180 mmol), and stirred at room temperature for 72 hours. It washed with distilled water (3×40 mL) and saturated NaCl aqueous solution (3×20 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The liquid was purified by column chromatography on silica gel using PE/EA (20:1) as eluent to afford white solid **UGF** (19.88 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.46 (s, 2H, furyl), 7.08-7.06 (d, 1H, phenyl), 6.83-6.80 (t, 2H, phenyl), 6.00-5.92 (m, 2H, CH_2CH=CH_2), 5.13-5.09 (m, 4H, CH_2CH=CH_2), 3.83 (s, 6H, OCH_3), 3.41-3.40(d, 4H, CH_2CH=CH_2); ^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) 155.9, 151.0, 146.6, 139.8, 137.0, 122.5, 120.9, 119.6, 116.2, 113.3, 56.0, and 40.0. MS (ESI) m/z: $[M+Na]^+$ calcd. for $C_{26}H_{24}O_7$ 471.1419, found: 471.1422. ATR-IR (cm^{-1}): 2840 ($\nu_{Ar\text{-}OCH_3}$), 1750 ($\nu_{C=O}$), 1640 ($\nu_{Ph\text{-}H}$), 1450 ($\nu_{C=CH_2}$), 1017 and 965 (furyl), 900-690 ($\nu_{Ar\text{-}H}$).

Synthesis of 2,5-Undecylenyl Furandicarboxylate (UF)

Under a nitrogen atmosphere, a 250 mL three-neck flask was charged with 10-undecenol (25.54 g, 150 mmol), FDCA (7.80 g, 50 mmol), DMAP (2.44 g, 20 mmol), and dry DCM (100 mL). The mixture was stirring at ice-water bath for 10 min, then added EDCI·HCl (23.29 g, 150 mmol), and stirred at room temperature for 3 days. It washed with distilled water (3×100 mL) and saturated NaCl aqueous solution (3×50 mL), and the organic layer was dried with Na_2SO_4, filtered, and concentrated under reduced pressure. The liquid was purified by column chromatography on silica gel using PE/EA (50:1) as eluent to afford a white product **UF** (14.97 g, 65%).

II. Supplementary Data and Discussion

Note S1. Characteristics of monomers

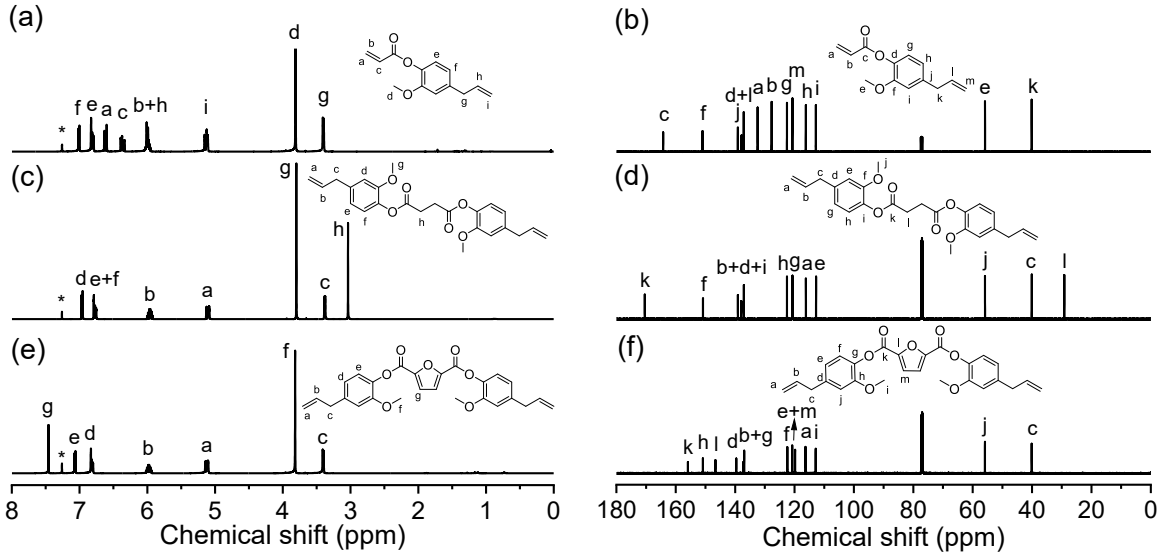

Figure S1. ^{1}H NMR (a,c,e) and ^{13}C NMR (b,d,f) spectra of **UGA** (a,b), **UGS** (c,d) and **UGF** (e,f) in $CDCl_3$.

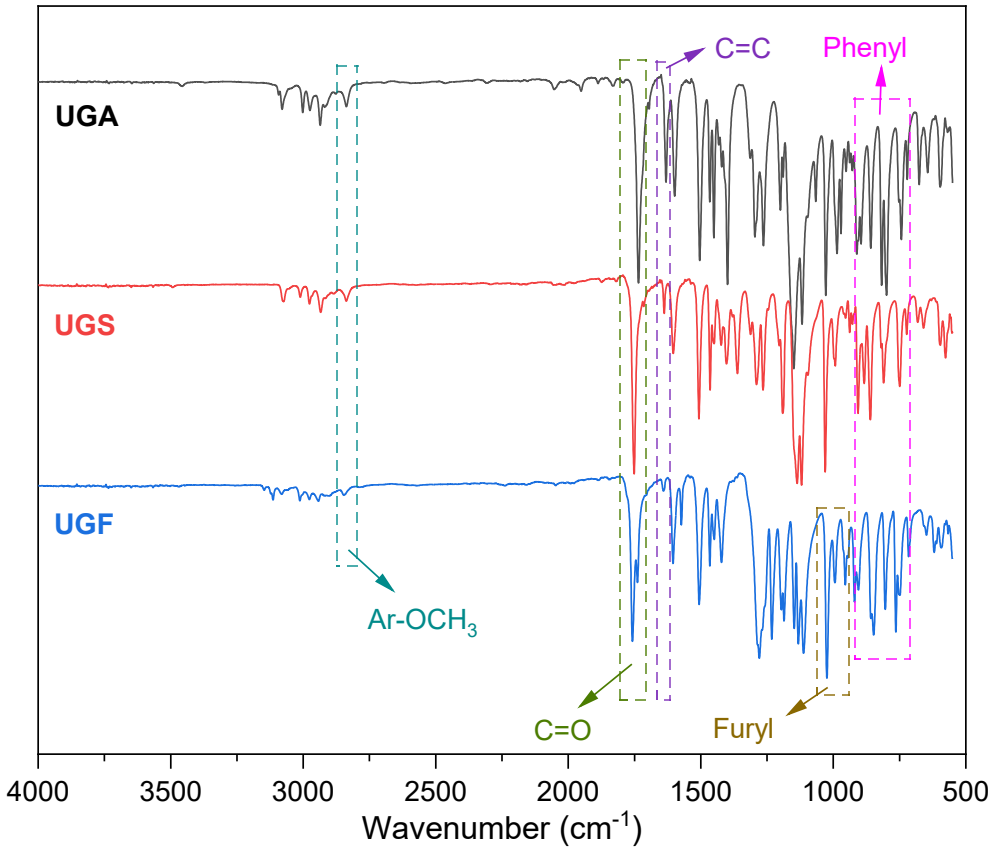

Figure S2. FT-IR spectra of UG-based monomers.

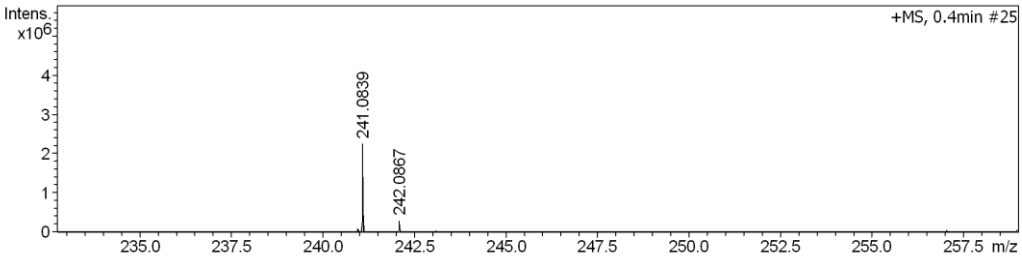

Figure S3. ESI mass spectrum of **UGA**.

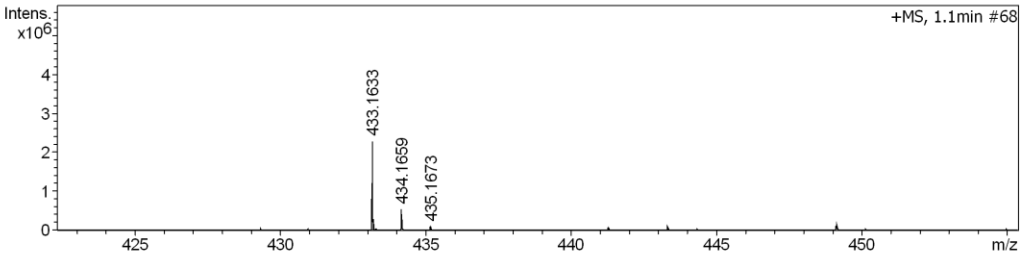

Figure S4. ESI mass spectrum of **UGS**.

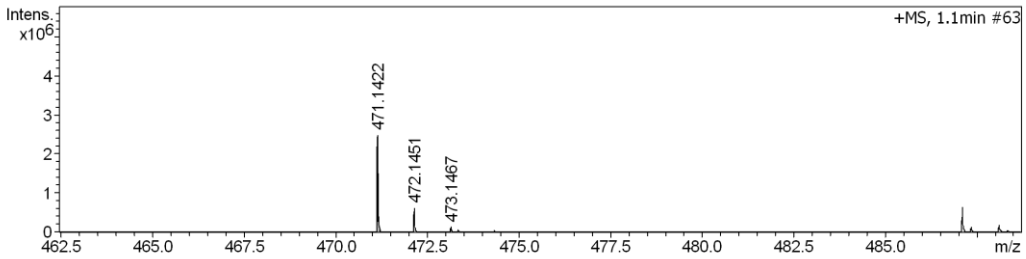

Figure S5. ESI mass spectrum of **UGF**.

Note S2. GPC traces of ADMET polymers

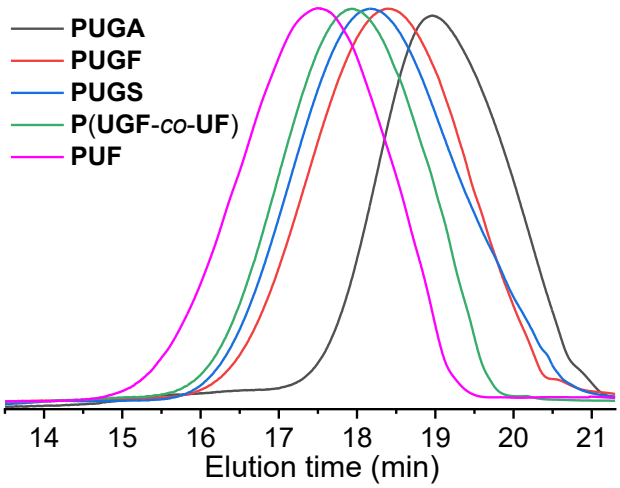

Figure S6. GPC traces of ADMET polymers.

Note S3. Characteristics of ADMET polymer

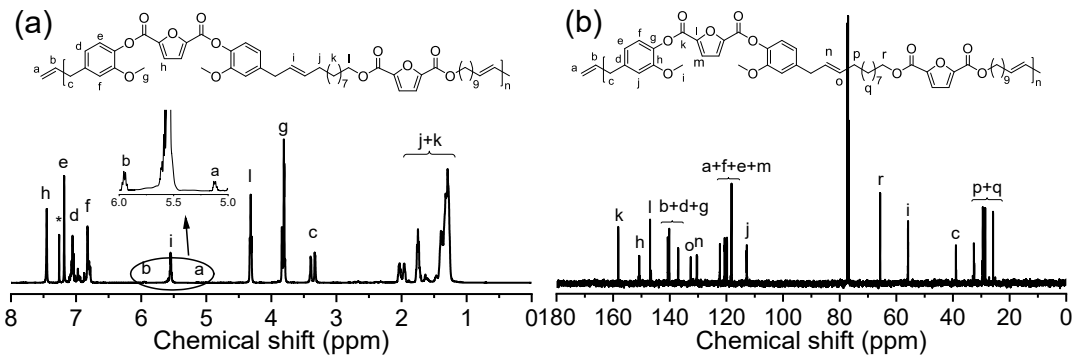

Figure S7. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of **P**(**UGF**-*co*-**UF**) in $CDCl_3$.

Note S4. Characterization of sulfur copolymer

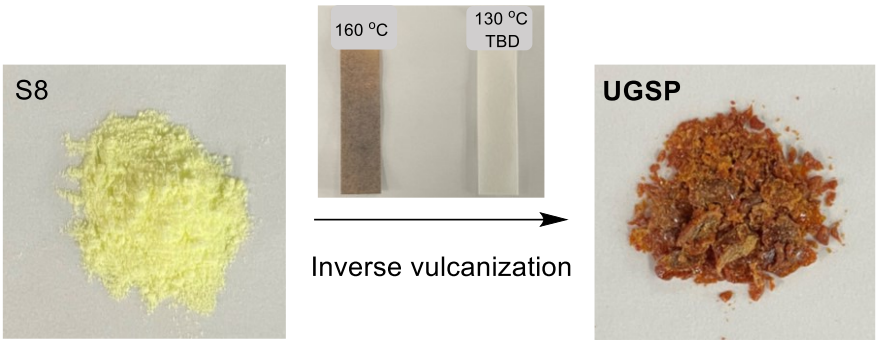

Figure S8. Photos of the S8 and **UGSP**. $Pb(Ac)_2$ test paper for the detection of H_2S production in inverse vulcanization under different reaction conditions (from left to right: 160 °C, 130 °C with TBD).

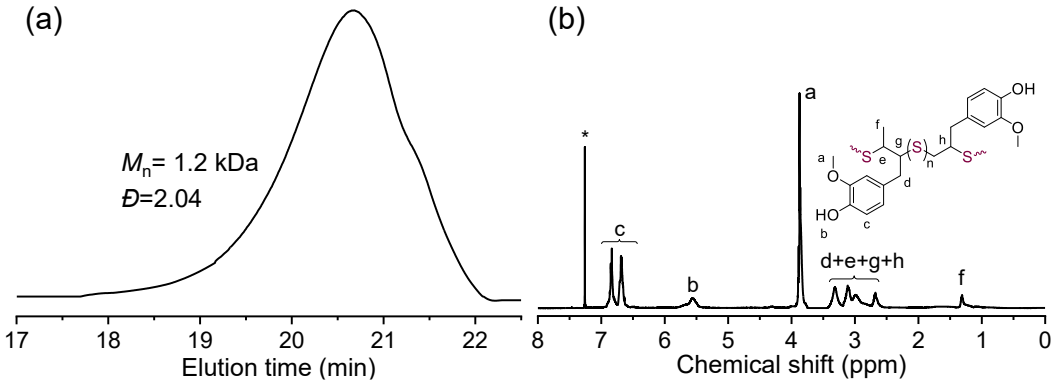

Figure S9. GPC trace (a) and ^1H NMR spectrum (b) of **UGSP**.

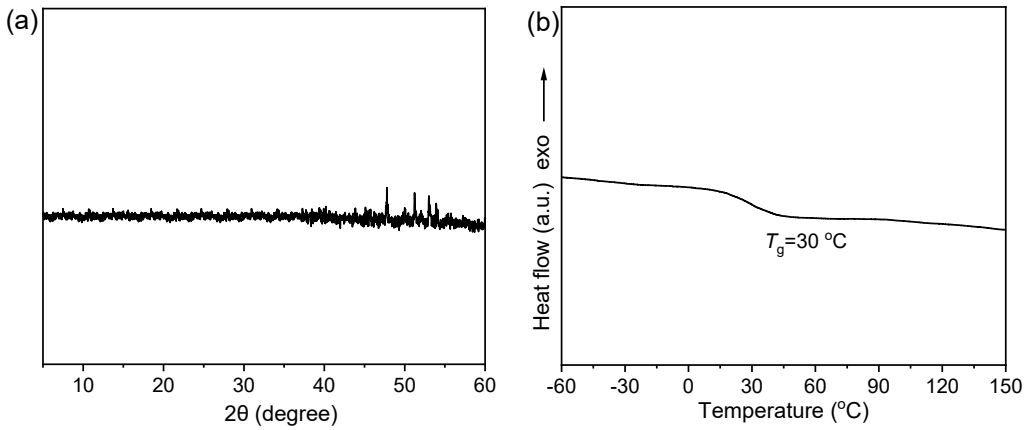

Figure S10. XRD pattern (a) and DSC curve (b) of **UGSP**.

Note S5. Characteristics of crosslinked and modified PUGS

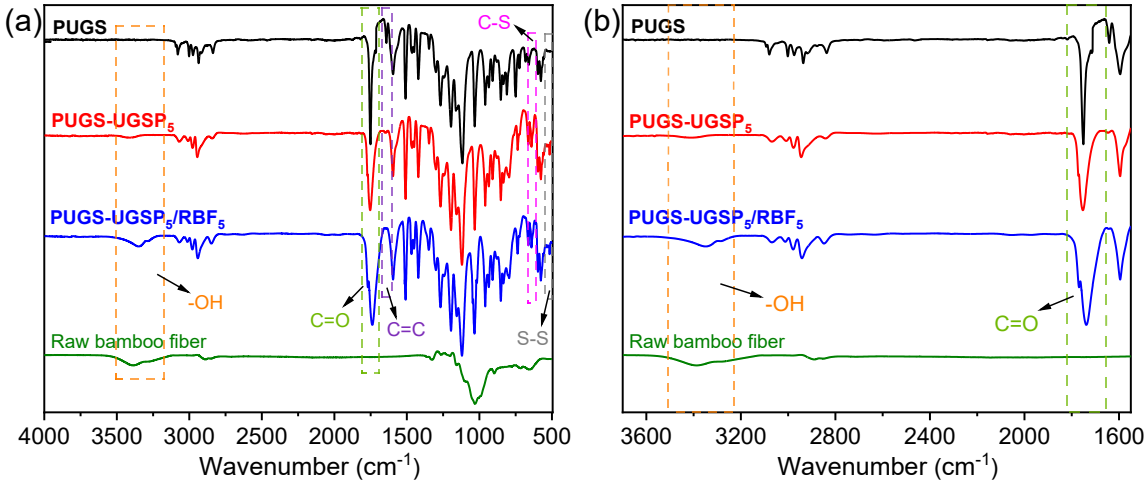

Figure S11. FT-IR spectra (a) and locally enlarged spectra (b) of **PUGS**, **PUGS-UGSP$_5$**, **PUGS-UGSP$_5$/RBF$_5$**, and raw bamboo fiber.

Note S6. Thermal properties of modified ADMET polymers

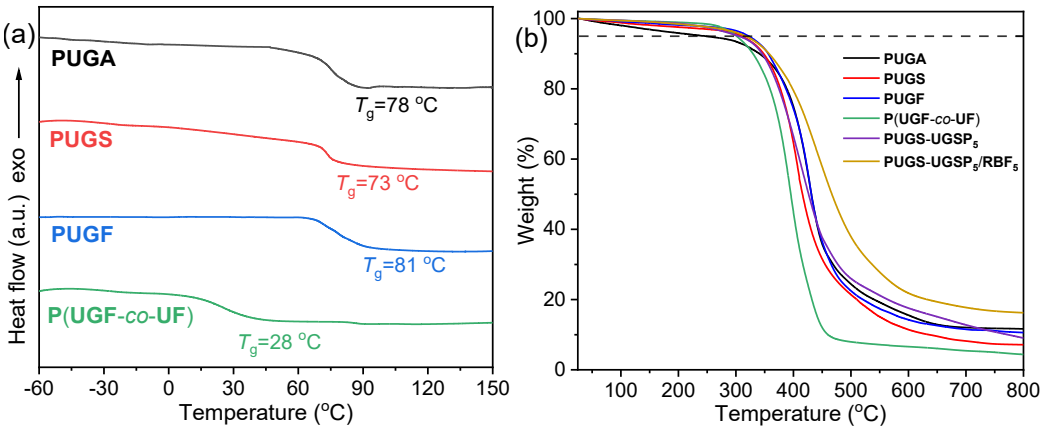

Figure S12. DSC (a) and TGA (b) curves of UG-based polymers.

Note S7. Mechanical properties of crosslinked and modified PUGS

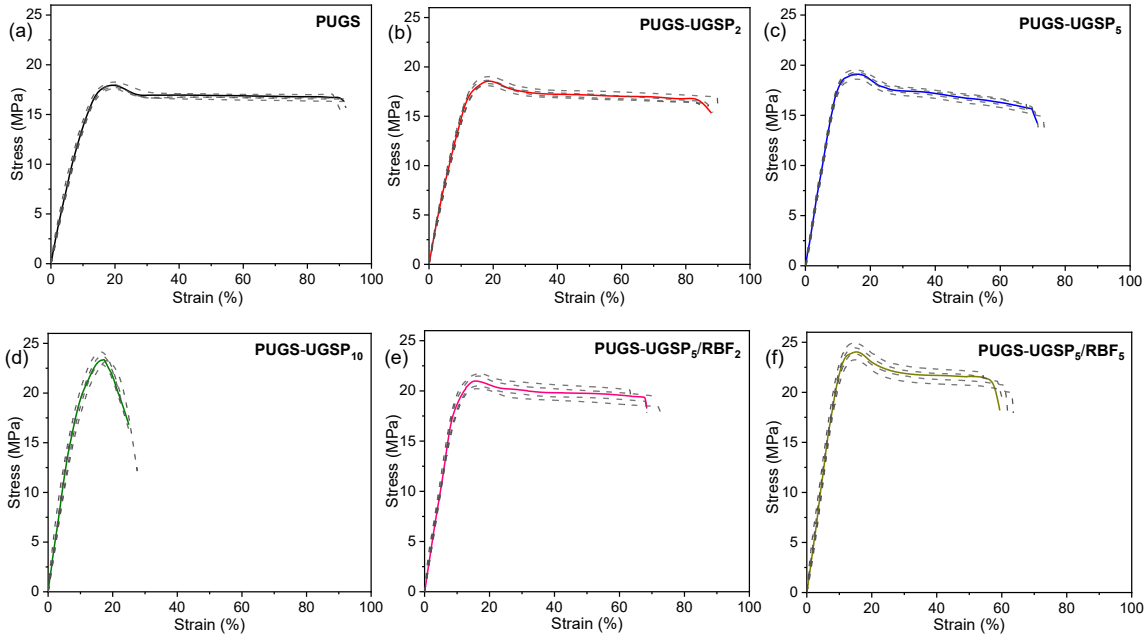

Figure S13. Stress-strain curves of **PUGS** (a), **PUGS-UGSP$_2$** (b), **PUGS-UGSP$_5$** (c), **PUGS-UGSP$_{10}$** (d), **PUGS-UGSP$_5$/RBF$_2$** (e), and **PUGS-UGSP$_5$/RBF$_5$** (f) strips include four replicates.

Note S8. Optical images of crosslinked and modified PUGS films

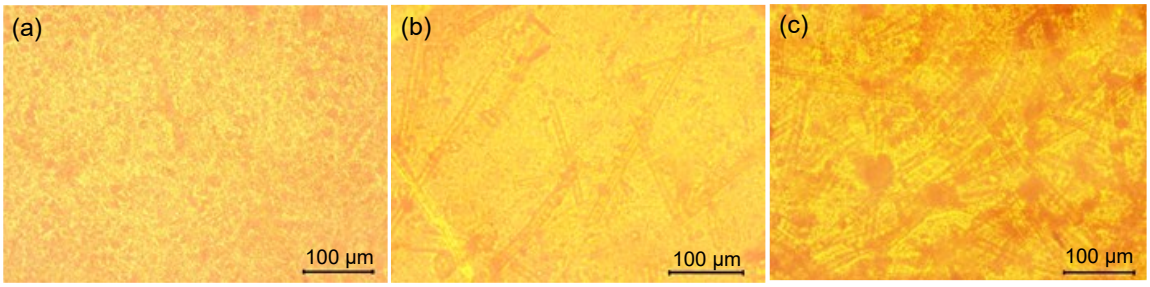

Figure S14. Optical images of **PUGS-UGSP$_5$** film (a), **PUGS-UGSP$_5$/RBF$_2$** film (b) and **PUGS-UGSP$_5$/RBF$_5$** film (c).

Note S9. Mechanical properties of other ADMET polyesters

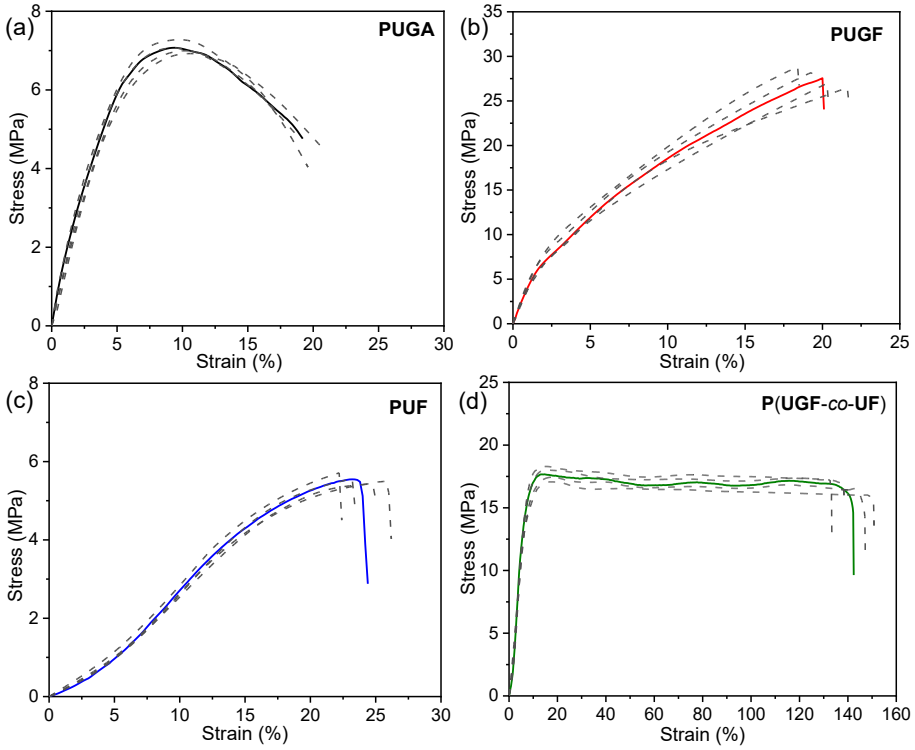

Figure S15. Stress-strain curves of **PUGA** (a), **PUGF** (b), **PUF** (c), and **P(UGF-*co*-UF)** (d) strips include four replicates.

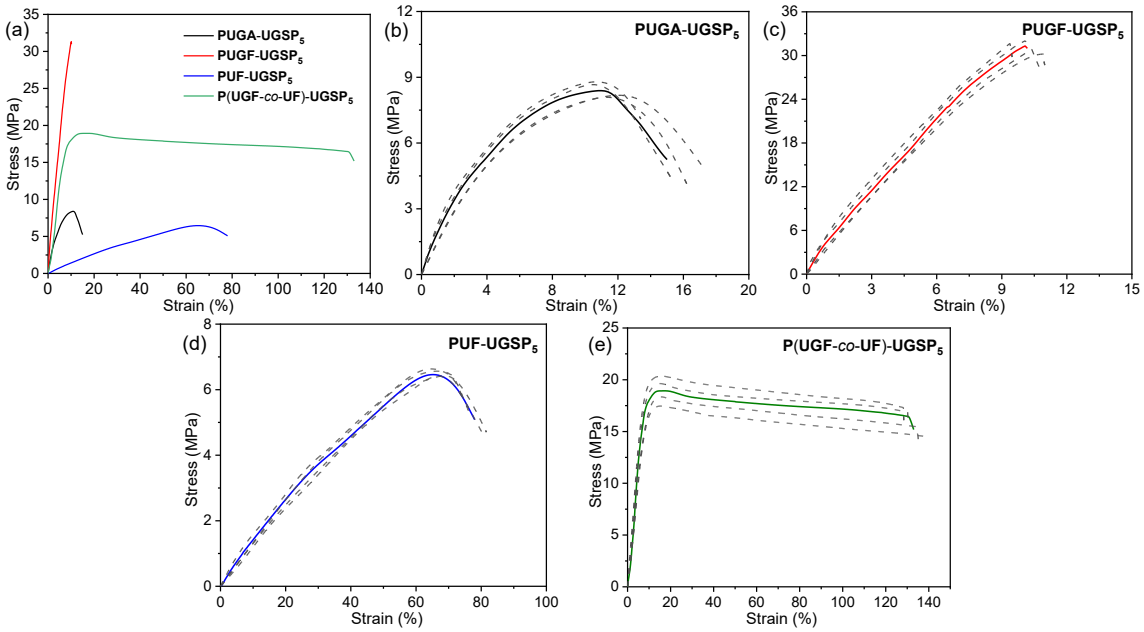

Figure S16. Stress-strain curves of **PUGA-UGSP$_5$**, **PUGF-UGSP$_5$**, **PUF-UGSP$_5$**, and **P(UGF-*co*-UF)-UGSP$_5$** strips (a) include four replicates (b-e).

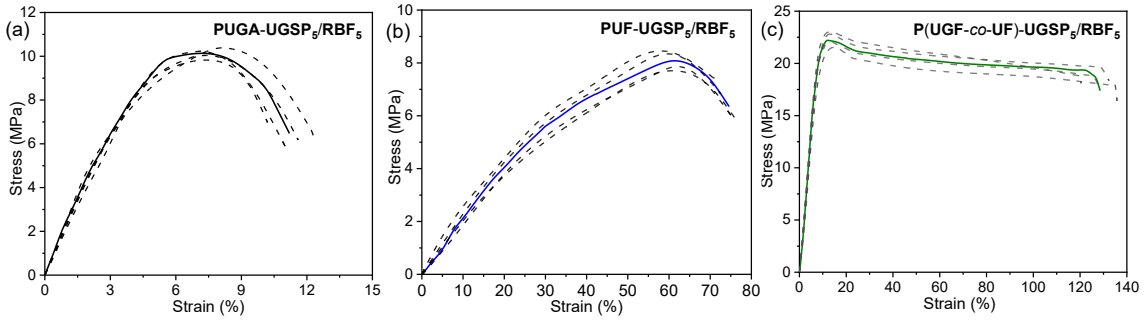

Figure S17. Stress-strain curves of **PUGA-UGSP$_5$/RBF$_5$** (a), **PUF-UGSP$_5$/RBF$_5$** (b), and **P(UGF-*co*-UF)-UGSP$_5$/RBF$_5$** (c) strips include four replicates.

Note S10. Disassembly of crosslinked modified PUGS-UGSP$_5$ film

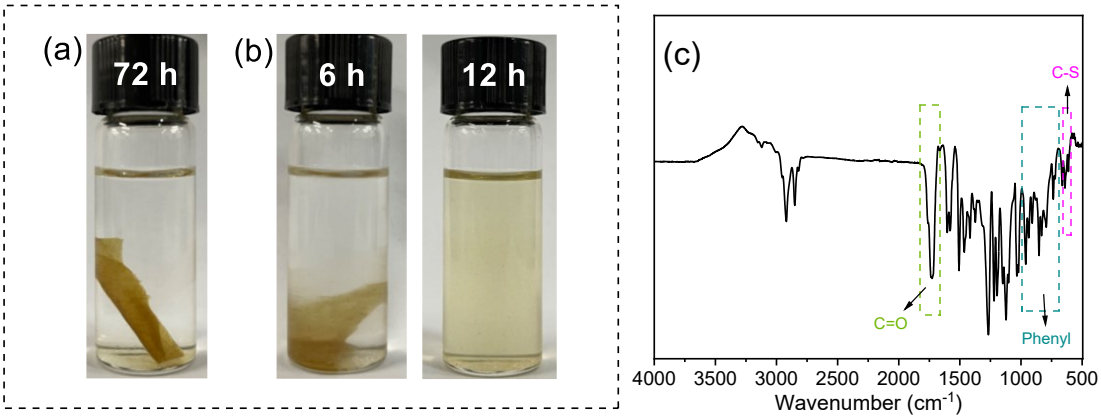

Figure S18. Photos of **PUGS-UGSP$_5$** in toluene after 72 h (a), and swollen in toluene solution of tris(2-carboxyethyl)phosphine (TCEP) (10 mmol L^{-1}) after 6 h and 12 h (b). FT-IR spectrum of **PUGS-UGSP$_5$** after decrosslinking process (c).

Note S11. Reprocessability of modified ADMET polyesters

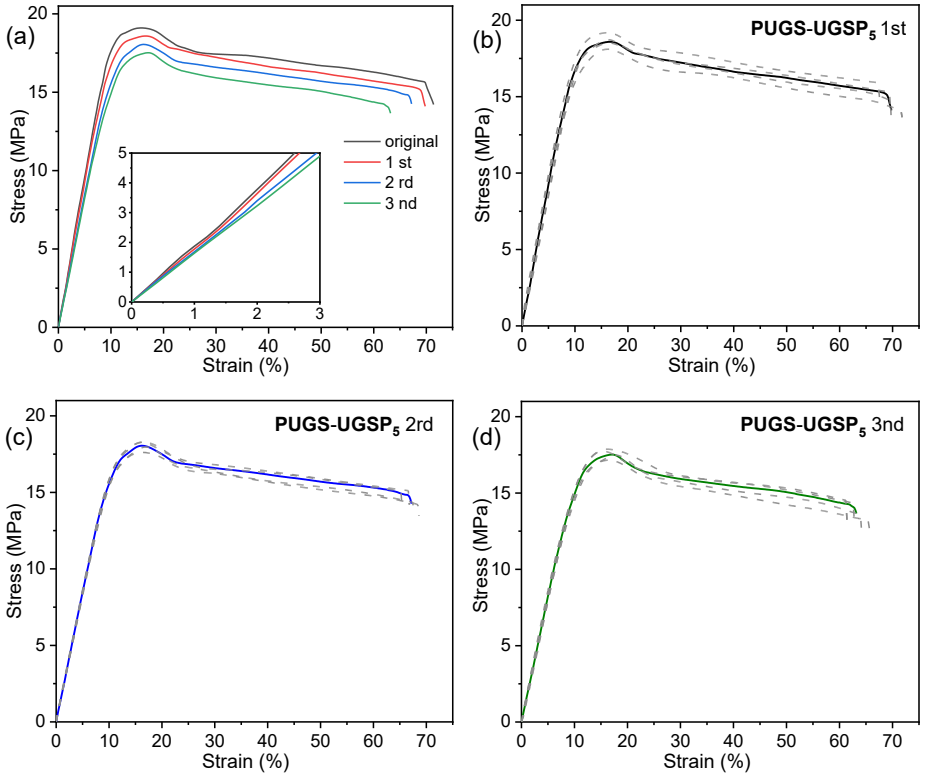

Figure S19. Stress-strain curves of **PUGS-UGSP$_5$** strips after multiple generations of reprocessing (a) include four replicates (b-d).

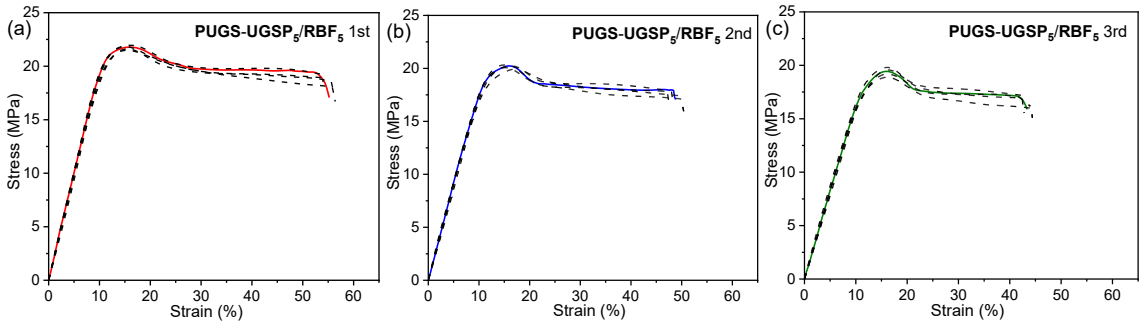

Figure S20. Stress-strain curves of **PUGS-UGSP$_5$/RBF$_5$** strips after multiple generations of reprocessing include four replicates (a-c).

Table S1. Mechanical properties of crosslinked polyester strips

sample	tensile strength (MPa)	elongation at break (%)	Young's modulus (MPa)	toughness (MJ m^{-3})
PUGS-UGSP$_5$ original	19.1±0.5	71±4	195.67	12.70
PUGS-UGSP$_5$ 1st[a]	18.6±0.6	70±3	188.32	10.92
PUGS-UGSP$_5$ 2nd[a]	18.1±0.2	67±2	169.74	10.13
PUGS-UGSP$_5$ 3rd[a]	17.5±0.4	63±4	163.25	9.15
PUGS-UGSP$_5$/RBF$_5$ original	24.0±1.0	59±5	238.01	12.13
PUGS-UGSP$_5$/RBF$_5$ 1st[a]	21.8±0.8	55±2	201.06	10.06
PUGS-UGSP$_5$/RBF$_5$ 2nd[a]	20.2±1.2	50±7	184.11	8.08
PUGS-UGSP$_5$/RBF$_5$ 3rd[a]	19.4±0.9	43±5	166.37	6.74
PUGA-UGSP$_5$/RBF$_5$[b]	10.0±0.4	10±1	240.98	0.77
PUGS-UGSP$_5$/RBF$_5$[b]	23.4±1.2	59±3	228.86	11.85
PUF-UGSP$_5$/RBF$_5$[b]	7.9±0.5	80±3	19.89	4.32
P(UGF-*co*-UF)-UGSP$_5$/RBF$_5$[b]	21.7±0.8	124±6	225.50	24.25

[a]The strips were cut into pieces and then reshaped at 150 °C and 10 MPa for 10 min.

[b]The strips were exposed to UV light for 72 h.

Note S12. Optical performance of ADMET polyester films

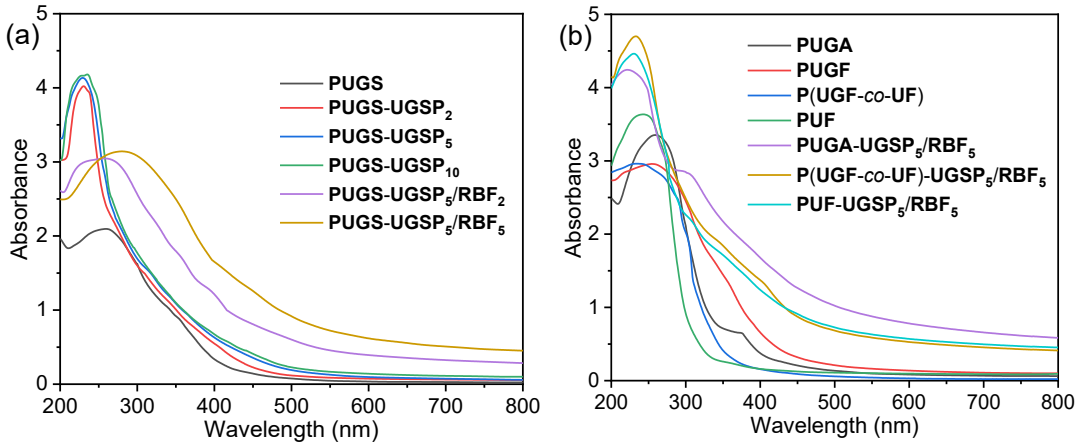

Figure S21. UV-vis spectra of **PUGS** and modified **PUGS** films (a), and other ADMET polyester films (b).

Table S2. T_{UVA}, T_{UVB}, and UPF values of ADMET polyesters and their composite films

entry	sample	T_{UVA} (%)	T_{UVB} (%)	UPF
1	**PUGS**	18.51	2.86	16.5
2	**PUGS-UGSP$_2$**	13.17	2.60	20.8
3	**PUGS-UGSP$_5$**	11.30	2.22	24.3
4	**PUGS-UGSP$_{10}$**	10.21	1.83	28.1
4	**PUGS-UGSP$_5$/RBF$_2$**	3.64	0.54	85.5
5	**PUGS-UGSP$_5$/RBF$_5$**	0.93	0.25	252.1
6	**PUGA**	20.49	0.98	21.0
7	**PUGF**	8.20	0.58	48.2
8	**PUF**	54.45	10.24	5.2
9	**P(UGF-*co*-UF)**	41.57	1.64	10.9
10	**PUGA-UGSP$_5$/RBF$_5$**	1.36	0.19	234.5
11	**PUF-UGSP$_5$/RBF$_5$**	2.59	0.41	117.0
12	**P(UGF-*co*-UF)-UGSP$_5$/RBF$_5$**	1.96	0.27	163.6
13[a]	**PUGS-UGSP$_5$/RBF$_5$**	0.93	0.27	246.9
14[a]	**PUGA-UGSP$_5$/RBF$_5$**	1.37	0.22	220.0
15[a]	**PUF-UGSP$_5$/RBF$_5$**	2.58	0.47	110.5
16[a]	**P(UGF-*co*-UF)-UGSP$_5$/RBF$_5$**	1.96	0.30	156.8

[a]Polyesters and their composite films were exposed to UV light for 72 h.

Note S13. Mechanical properties of modified ADMET polyesters after 72 h of UV irradiation

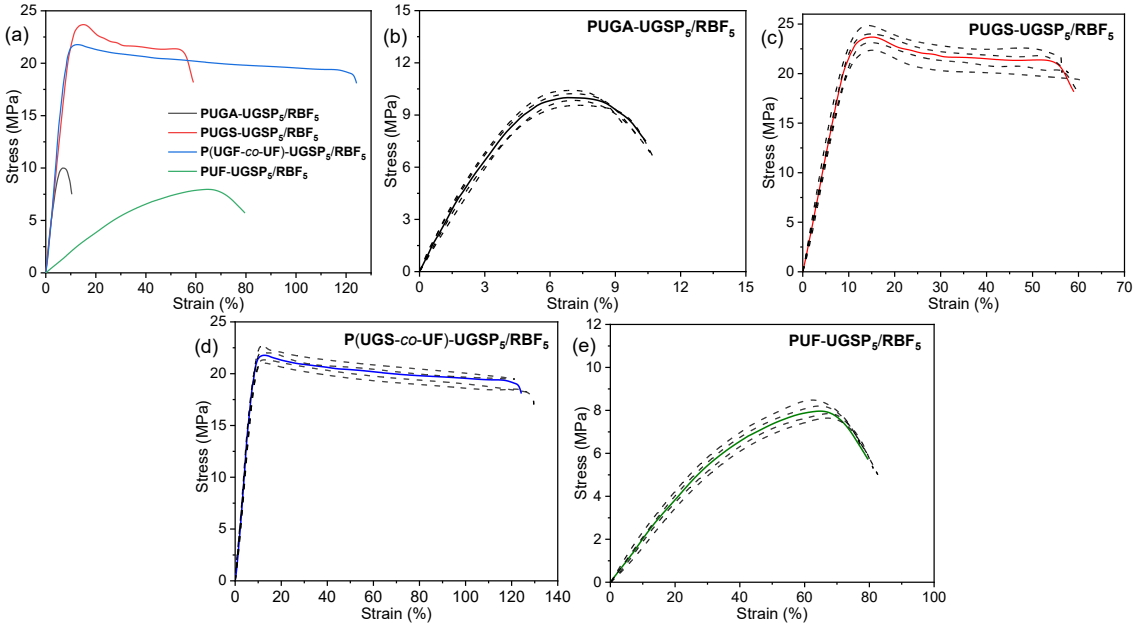

Figure S22. Stress-strain curves of **PUGS-UGSP$_5$/RBF$_5$** strips after 72 h of UV irradiation (a) include four replicates (b-e).