Electronic supplementary information

Malleable and thermally recyclable polyurethane foam

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A. Materials and General methods

Materials. Polyether polyols (PPG, average functionality of 2.0, OH content of 56 mg of KOH/g, technical pure grade), toluene diisocyanate (TDI 80/20, technical pure grade), catalysts T9 (stannous octoate) and A33 (33% triethylene diamine solution), silicon oil (SO) were obtained from Yantai Wanhua Polyurethanes co., Ltd. Polysulfide oligomer (PSO, AR grade) with molecular weight of 800 g/mol was supplied by Micxy Chemical Co., Ltd., Chengdu, China.

Preparation of PU foams. PU foam was synthesized by a solvent free, one-pot and free-rise method. Taking PSUF-10 for an example, PPG (90 g), PSO (10 g), catalysts T9 (0.2 g) and A33 (0.4 g), surfactant (SO, 1g), and distilled water (3 g) were first mixed homogeneously in a 1 L plastic beaker with a mechanical stirrer for 5 min. Subsequently, TDI 80/20 (42.9 g) was added into beaker with vigorous stirring (1000 rpm) for 15 s. Thereafter, the mixtures were immediately poured into an open plastic mold (30 × 20 × 10 cm^3) to generate free-rise foam. The foam was cured under ambient conditions for 24 h. The formulations of all the PU foams are shown in Table S1. The NCO/OH molar ratio was 1.05.

Instruments and characterization. FT-IR spectra were recorded on a RF-5301PC spectrophotometer (Shimadzu, Japan) from 4000-400 cm^{-1}, and the resolution as well as scanning time was 4 cm^{-1} and 32, respectively.

The cross sections of the samples were observed with tungsten filament electron scanning microscope (JSM-6510, JEOL) at an accelerating voltage of 10 kV.

Stress relaxation was conducted using a TA DHR-1 rotational rheometer. The disk-like

sample sheets (diameter: 25 mm, thickness: 1 mm) prepared by compression molding were used for the testing. The sample between the two plates was first equilibrated for 5 minutes at the predetermined temperature, and then a 1% strain step was used. The variation of storage modulus with time was recorded for stress relaxation analysis.

Testing. The density of PU foams with size of more than 100 cm^3 was measured according to ISO 845:2006. Average results of five measurements were recorded for all the samples. Resilience rate of the PU foams was characterized in accordance with standard ISO 1856:2000. The size of each specimen was 50 × 50 × 25 mm^3 (length × width × thickness) and average results of five measurements were reported for all the samples. The sample was compressed to its half-thickness, fixed and then placed in a 70 ℃ oven for 22 h. Thereafter, the sample was recovered at room temperature for 0.5 h after moving out of the oven. The resilience rate was calculated by the equation:

Resilience rate (%) = (compression strain-residual strain)/compression strain

Tensile testing of RPUSFs was conducted by an MTS E44 Universal Testing machine at room temperature with a crosshead rate of 10 mm min^{-1}. Dumbbell-shaped specimen with width and thickness of 4 and 0.5 mm were used for the tensile testing. Five measurements were carried out for each sample and the average results were reported.

Dynamical mechanical analysis was performed using a DMA 1 (METTLER TOLEDO Instruments). The samples were measured under a tensile mode with the temperature range of -90 ℃ to 70 ℃. The frequency and heating rate were 1 Hz and 3 ℃ min^{-1}, respectively. The length, width and thickness of the sample was 35, 6 and 0.5 mm, respectively.

Differential scanning calorimetry (DSC) curves were recorded on a NETZSCH instrument DSC-214 from -100 ℃ to 20 ℃ at a heating rate of 10 ℃/min under a N_2 atmosphere.

The thermal stability of the samples was studied by a TA Instruments TGA Q500 from room temperature (30 ℃) to 600 °C at a heating rate of 10 °C/min under N_2 atmosphere. Thermogravimetric analysis is characterized by hot-pressed samples. The control sample is the hot-pressed PUF, which is named RPUF here.

The gel fraction and swelling ratio were measured via solvent immersion. The samples were immersed in 25 ml N, N-Dimethylformamide for three days to dissolved the uncross-linked parts. The initial weight of the sample was recorded as W_0. After removing the surface solvent with filter paper, the weight of the swollen sample was determined as W_1. The insoluble parts were vacuum-dried at 100 ℃ for 24 h to obtain the dried samples, as W_2. The swelling ratio (S_r) of the sample was computed by

$$S_r = \frac{W_1 - W_0}{W_0} \times 100\%$$

The gel fraction (G_f) of the sample was computed by

$$G_f = \frac{W_2}{W_0} \times 100\%$$

B. Characterization Figures

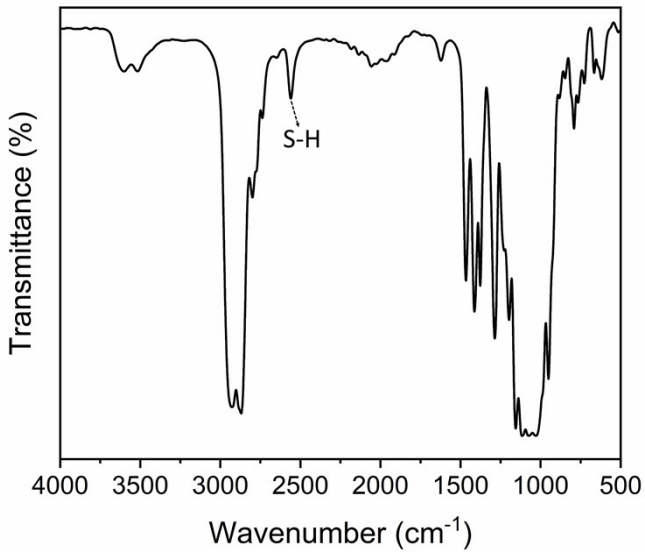

Fig. S1 FT-IR spectrum of polysulfide oligomer (PSO).

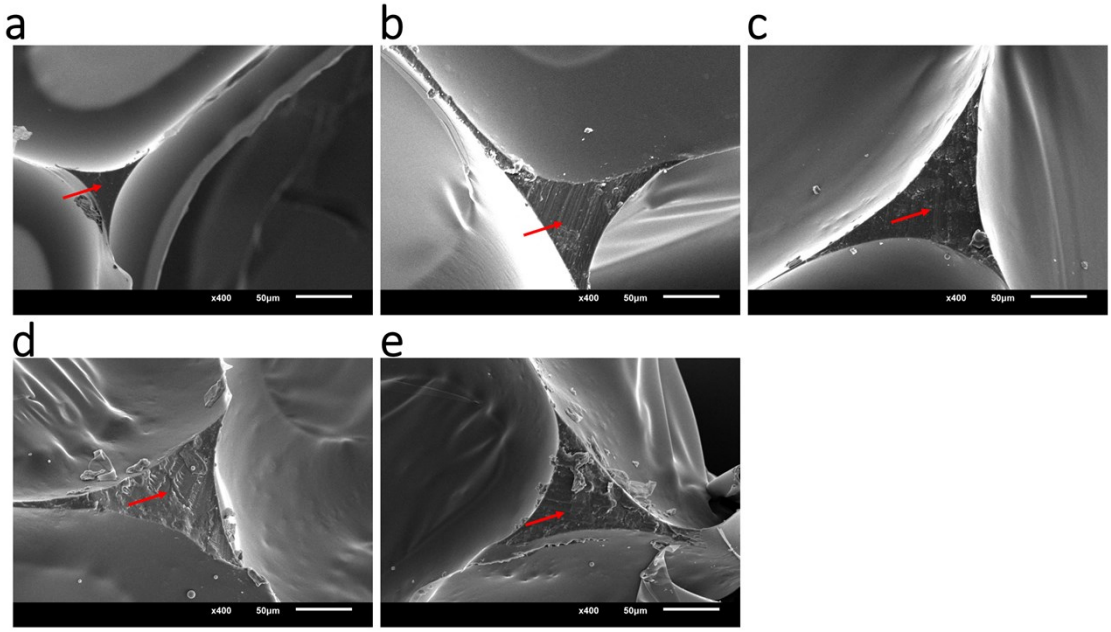

Fig. S2 SEM images with ×400 magnification of PUF (a), PUSF-10 (b), PUSF-20 (c), PUSF-30 (d), and PUSF-40 (e) showing the size of strut joint (as designated with red arrow).

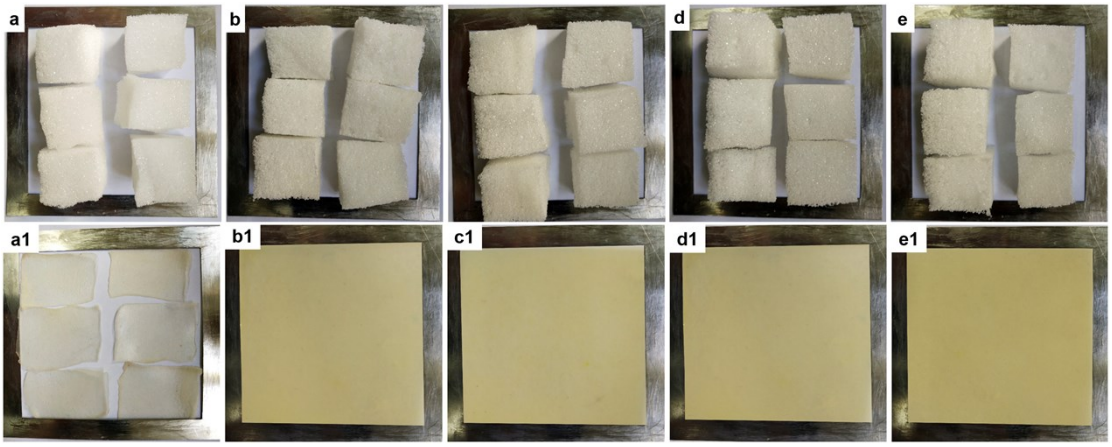

Fig. S3 The photographs of original PU foams: PUF (a), PUSF-10 (b), PUSF-20 (c), PUSF-30 (d), and PUSF-40 (e) and of the recycled PU films: RPUF (a1), RPUSF-10 (b1), RPUSF-20 (c1), RPUSF-30 (d1), and RPUSF-40 (e1).

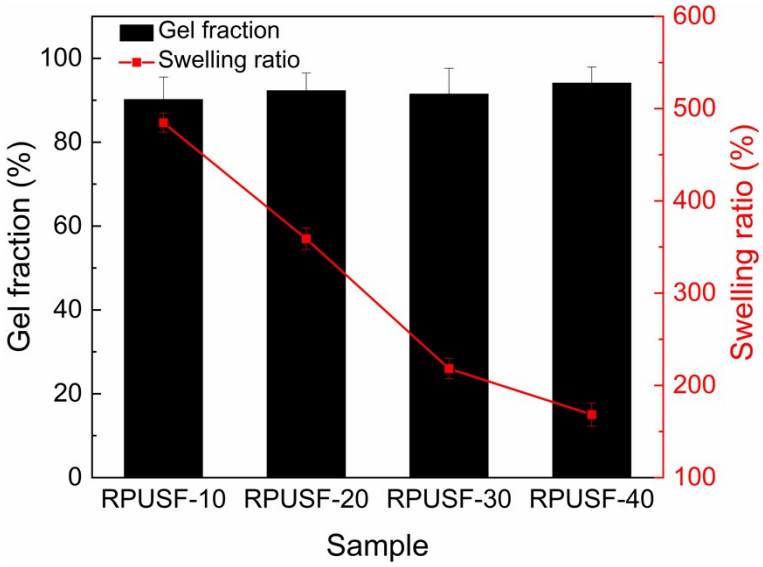

Fig. S4 Gel fraction and swelling ratio of recycled PU films from malleable PU foams with different compositions.

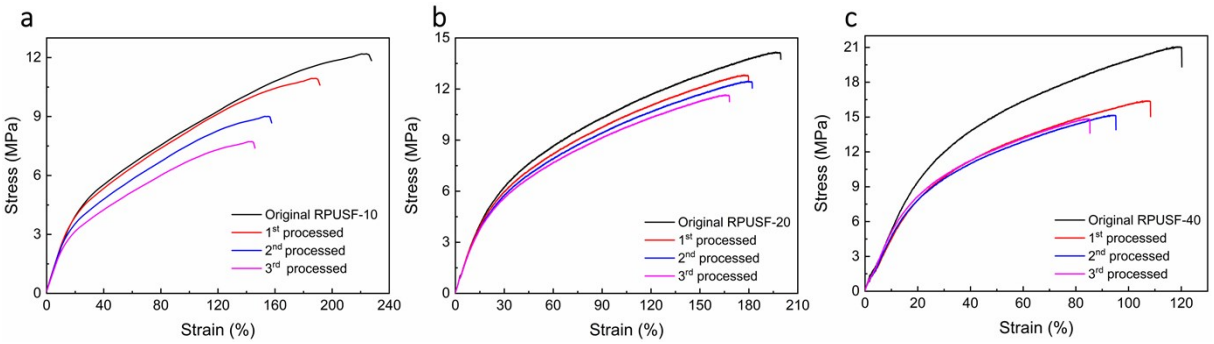

Fig. S5 Stress-strain curves of original and reprocessed RPUSF-10 (a), RPUSF-20 (b), and RPUSF-40 (c).

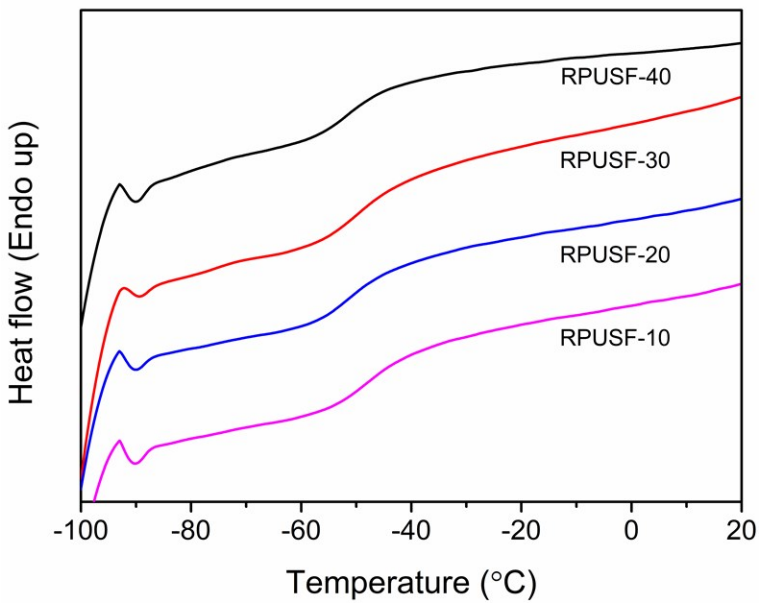

Fig. S6 DSC heating scans of RPUSFs.

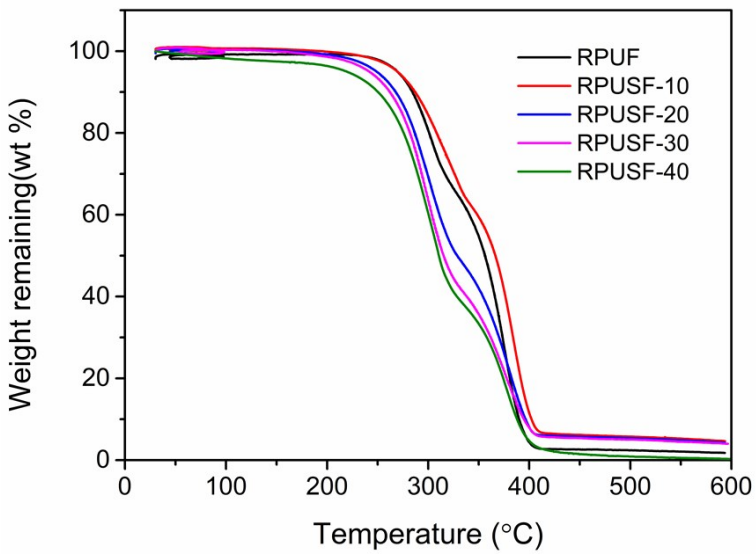

Fig. S7 TGA curves of the RPUF and RPUSFs.

C. Characterization Tables

Table S1. Formulations of PU foams.

Sample	PPG (g)	PSO (g)	A33 (g)	T9 (g)	SO (g)	Water (g)	TDI (g)
PUF	100	0	0.4	0.2	1	3	41
PUSF-10	90	10	0.4	0.2	1	3	42.9
PUSF-20	80	20	0.4	0.2	1	3	44.8
PUSF-30	70	30	0.4	0.2	1	3	46.8
PUSF-40	60	40	0.4	0.2	1	3	48.6

Table S2. Tensile strength (σ), elongation at break (ε), and Young's modulus (*E*) of recycled PU films.

Sample	σ (MPa)	ε (%)	*E* (MPa)
RPUSF-10	12.2±2.1	225.8±12.1	22.9±2.4
RPUSF-20	14.1±3.3	199.5±10.3	34.5±8.3
RPUSF-30	17.4±4.1	191.7±8.1	40. 4±3.2
RPUSF-40	21.0±1.1	120.1±5.3	60.6±5.2

Table S3. Tensile strength (σ), elongation at break (ε), Young's modulus, and gel fractions (G_f) of reprocessed RPUSF-10 films.

Processing No.	σ (MPa)	ε (%)	*E* (MPa)	G_f(%)
1st	10.4±1.6	187.8±8.6	27.3±5.1	89.2
2nd	9.0±2.3	154.1±2.6	30.1±2.9	90.1
3rd	7.5±1.3	143.7±1.8	28.6±1.6	91.0

Table S4. Tensile strength (σ), elongation at break (ε), Young's modulus, and gel fractions (G_f) of reprocessed RPUSF-20 films.

Processing No.	σ (MPa)	ε (%)	*E* (MPa)	G_f(%)
1st	12.0±3.1	178.9±4.1	32.8±1.9	90.4
2nd	12.6±2.3	180.2±1.9	31.6±2.8	92.0
3rd	11.2±1.7	167.2±5.6	30.2±4.9	89.4

Table S5. Tensile strength (σ), elongation at break (ε), Young's modulus, and gel fractions (G_f) of reprocessed RPUSF-30 films.

Processing No.	σ (MPa)	ε (%)	*E* (MPa)	G_f(%)
1st	16.2±1.9	181.3±2.6	41.1±2.1	91.6
2nd	17.2±2.6	192.6±5.8	37.8±4.7	92.1
3rd	16.6±3.3	179.2±4.5	43.5±3.6	90.8

Table S6. Tensile strength (σ), elongation at break (ε), Young's modulus, and gel fractions (G_f) of reprocessed RPUSF-40 films.

Processing No.	σ (MPa)	ε (%)	*E* (MPa)	G_f(%)
1st	15.9±3.6	108.2±1.0	49.6±2.1	94.6
2nd	14.7±2.3	95.5±2.6	49.3±1.4	93.4
3rd	14.8±2.2	85.3±4.1	50.6±4.4	92.8