Supporting information

Bio-Based, Robust and Recyclable Thermoset Polyester Elastomer by Using Inverse Vulcanised Polysulfide as Crosslinker

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Materials

1,4-Butanediol (BDO), 1,3-propanediol (PDO), tetrabutyltitanate (TBT) were obtained from Alfa Aesar. Itaconic acid (IA), succinic acid (SA), sebacic acid (SeA), hydroquinone and orthophosphoric acid were provided by Guangfu Fine Chemical Institute of Tianjin. Styrene (99%), 1,10-decanedithiol (DT, 96%), hexanethiol (96%), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 99%) were purchased from Beijing InnoChem Science & Technology Co. Ltd., Beijing, China. Sulfur and silica were industrially available. All the chemicals are used as received.

Synthesis of linear and unsaturated polyester elastomer (BPE).

BPE was synthesized via a two-step method: esterification and polycondensation. First, 1,4-butanediol (0.165 mol), 1,3-propanediol (0.165 mol), sebacic acid (0.1275 mol), succinic acid (0.1275 mol) and itaconic acid (0.03 mol), inhibitors of hydroquinone (0.04 wt% relative to the reactants) and orthophosphoric acid (0.01 wt% relative to the reactants) were reacted at 180 °C under nitrogen for 2 h. Then, catalyst TBT (0.05 wt% relative to the reactants) was added and the mixture was maintained at 220 °C with the pressure reduced to 300 Pa under stirring until "Weisenberg effect" was observed. The resultant was dissolved in chloroform and precipitated with methanol, followed by vacuum dried at 40 °C overnight to product BPE.[1]

Synthesis of inverse vulcanised sulfur-polymer (SP).

Elemental sulfur (14.0 g, 436 mmol) was added to a 100 mL flask and maintained at 130 °C until a yellow uniform liquid formed. Styrene (6.0 g, 58 mmol) was then added to the molten sulfur in a dropwise fashion. The reaction mixture was stirred at 130 °C for 6 h. After the reaction, the mixture was dissolved in 40 mL of tetrahydrofuran, and the solution was cooled to -20 °C to precipitate unreacted sulfur. Then the supernatant was evaporated to yield an orange copolymer (13.6 g, 67.7% yield).

Preparation of SP-cured BPE samples (BPE/SP-x)

100 g of BPE, 0.3 g of DBU and varied amount of SP (1.0, 1.5, 2.0, 3.0 g) were mixed using an open two-roll mill. The obtained compounds were subjected to compression molding at 160 °C for

optimum time to produce SP-cured BPE. The code BPE/SP-x means SP-cured BPE, where x is the weight fraction of SP relative to BPE.

Preparation of 1,10-decanedithiol-cured BPE sample without S-S bonds (BPE/DT).
For comparison, a control sample without S-S bonds was prepared by crosslinking BPE with 1,10-decanedithiol (DT). Due to the high activity of thiols in 1,10-decanedithiol, the crosslinking of BPE occurs during the mechanical mixing process before molding. Alternatively, solution blending method was adopted by dissolving BPE (10 g), 1,10-decanedithiol (0.2 g) and DBU (0.03 g) in 40 mL of trichloromethane under stirring. Then the mixture solution was poured into a PTFE mold and placed in a fume hood to evaporate the solvent. The yielded film was cured at 80 ^{o}C overnight to produce DT-crosslinked BPE (BPE/DT).

Preparation of SP-cured silica-filled BPE composite (BPE/silica composite).
BPE/silica composite was prepared according to the similar protocols for the preparation of BPE/SP-x. The formulation is as follow: BPE 100 g; SP 3.0 g; DBU 1.0 g; silica 30.0 g. DBU dosage is increased due to the adsorption of DBU onto silica.

Characterizations
^{1}H NMR spectra were recorded using a Bruker AVANCE III HD 600. The samples were dissolved in CDCl$_3$ and TMS was used as an internal standard. Fourier transform infrared (FTIR) spectra were collected using a Bruker Vertex 70 FTIR spectrometer. Cross-linking kinetics were determined at 160 °C on a U-CAN UR-2030 vulcameter. The tensile tests were performed on a Gotech AI-7000 S universal testing machine following ISO standard 37-2005. At least five specimens were measured for each sample, and the average values and standard deviations were given. Dynamic mechanical analysis (DMA) and stress relaxation measurements were performed on a TA-Q800 DMA apparatus. DMA temperature sweeping tests were conducted under a tensile mode with a dynamic strain of 0.5%. The temperature was increased from −80 to 120 °C at 3 °C/min and the frequency was 1 Hz. For stress relaxation measurements, a constant strain of 2 % was applied and the stress decay was monitored over time. Molecular weights of SP and BPE were determined by gel permeation chromatography (GPC) using a Waters 2414 series system in tetrahydrofuran and calibrated with the polystyrene standard. X-ray spectroscopy (XPS) analysis was performed on an Escalab Xiþ equipped with Al Ka radiation source. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF MS) measurement was performed on a Bruker Autoflex III Smartbeam MALDI-TOF mass spectrometer (Bruker, Germany). Thermal gravimetric analysis (TGA) was performed on a TA Q50 thermogravimetric analyzer under a nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted on a TA DSC25 machine by heating the samples from -80 to 140 ^{o}C with 10 ^{o}C/min. Optical microscopy images were recorded using a SOPTOP CX40MRT instrument. Transmission electron microscopy (TEM) was performed on a JEM-2100F instrument. Scanning electron microscopy (SEM) was observed by using a Hitachi SU-70 instrument.

Crosslinking density and sol fraction were determined based on equilibrium swelling tests by immersing the samples in toluene for 72 h. After reaching the swelling equilibrium, the solvent was wiped off quickly from the sample surface using filter paper, and the samples were immediately weighed. Finally, the samples were dried in a vacuum oven at 60 °C until constant weight. Three

specimens were measured for each sample, and the average value and standard deviation were calculated. The sol fraction is determined as $(m_0 - m_2)/m_0$, where m_0 is the weight of the sample before swelling, m_2 is the weight of the deswollen sample.

The crosslinking density (V_e) is calculated based on Flory-Rehner equation (1)

$$V_e = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_s(V_r^{1/3} - V_r/2)} \tag{1}$$

where χ is the Flory-Huggins polymer solvent interaction parameter, V_s is the molar volume of the solvent. V_r is the volume fraction of BPE in the swollen gel, which is calculated by the following equation (2):

$$V_r = \frac{m_2/\rho_r}{m_2/\rho_r + (m_1 - m_2)/\rho_s} \tag{2}$$

where m_1 is the weight of the swollen sample, ρ_r and ρ_s are the densities of the BPE and solvent, respectively.
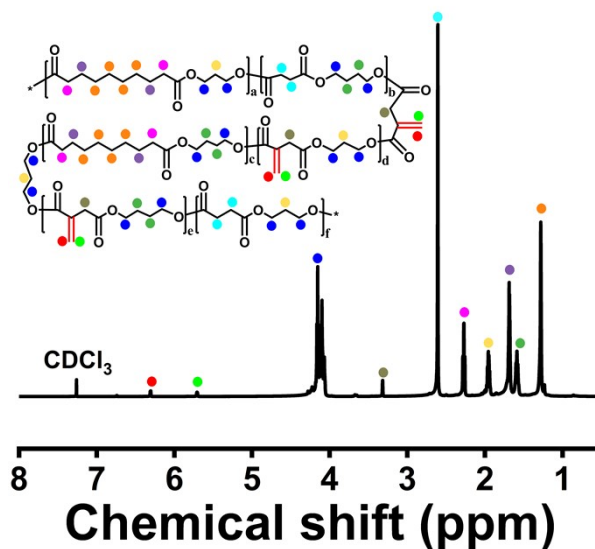
Fig. S1 ^{1}H NMR spectrum of BPE.

In the ^{1}H NMR spectra of SP, the signals at 6.65, 5.68 and 5.17 ppm related to the protons of the vinyl groups in styrene disappear, and a broad peak from 3.0-4.8 ppm is present, which corresponds to the protons in the –S–CH– fragments, indicating the addition of sulfur onto the vinyl groups. The signals at 1.5-1.7 ppm may be due to the protons of the alkyl groups not bonded to the polysulfide chains. In the DSC curve of SP, the melting peak related to S_8 is absent and a glass transition at -1.5 °C is observed, which confirms the conversion of crystalline sulfur into sulfur co-polymer.
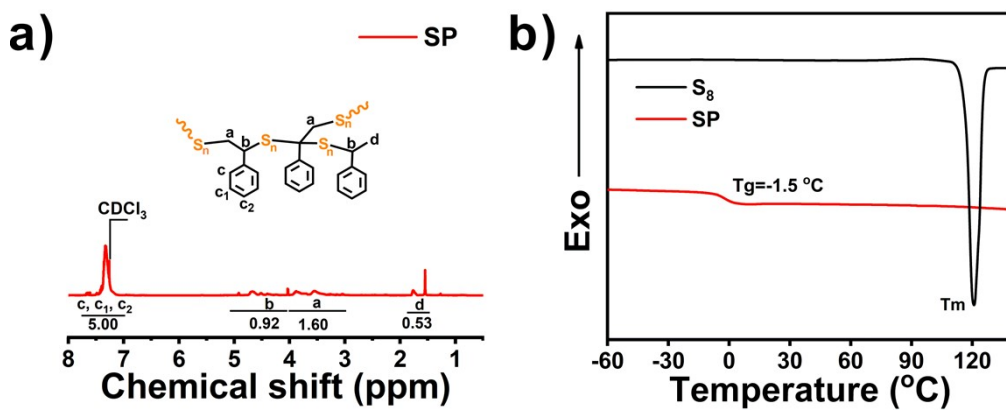
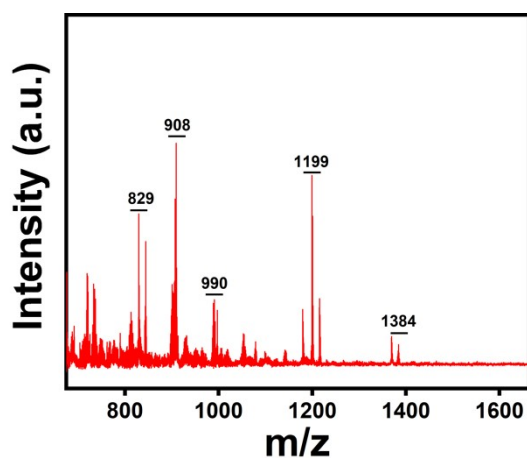**Fig. S2** (a) ^{1}H NMR spectrum of SP. (b) DSC curves of SP and S_8.

Fig. S3. MALDI-TOF MS spectrum of SP.

From the high-resolution S 2p XPS spectrum of SP, the ratio of S-S to C-S in SP is determined to be 1.06. Accordingly, the S rank is calculated to be ~4.1.[2, 3]
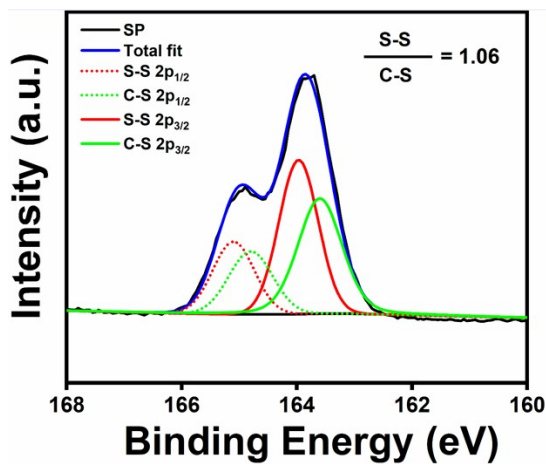

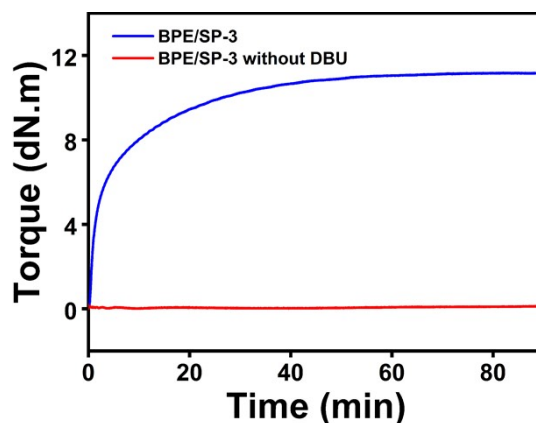**Fig. S4**. High-resolution S 2p XPS spectrum of SP.

Fig. S5 Evolution of torque versus time at 160 °C for BPE/SP-3 and BPE/SP-3 without adding DBU.

The model experiment was performed by reacting SP (5 g) with dibutyl itaconate (5 g) under the catalysis of DBU (0.1 g) at 130 °C for 15 min to substantiate whether depolymerization occurs during the crosslinking process. The ^{1}H NMR spectra were displayed in Fig. S6a. In the ^{1}H NMR spectrum of the reaction mixture, the signals related to CH_2=CH- for dibutyl itaconate disappear, and new signals within 2.0-3.0 ppm related to the protons in S-CH fragments are observed,[4] revealing the addition of S-S bonds onto C=C bonds. In addition, no singles related to itaconate acid or butanol are found, indicating that the carbon-centered enolate anion intermediate does not lead to the degradation of ester groups.

Moreover, the FTIR spectra of dibutyl itaconate and reaction mixture were shown in Fig. S6b. In the FTIR spectrum of the reaction mixture, the band at 1640 cm^{-1} related to the C=C stretching vibrations of dibutyl itaconate disappears, and the band at 510 cm^{-1} corresponded to S-S stretching vibrations is observed, further indicating the addition of SP onto C=C bonds of dibutyl itaconate and existence of S-S linkages in the reaction mixture.

Collectively, the results from the model experiment indicate the addition of S-S bonds onto C=C bonds of dibutyl itaconate and no degradation of ester groups during the reaction. Admittedly, the detailed mechanism is complicated, because sulfur has multifaceted chemistry[5] and DBU is both basic and nucleophilic, which may make the reaction follow multi-paths[6]
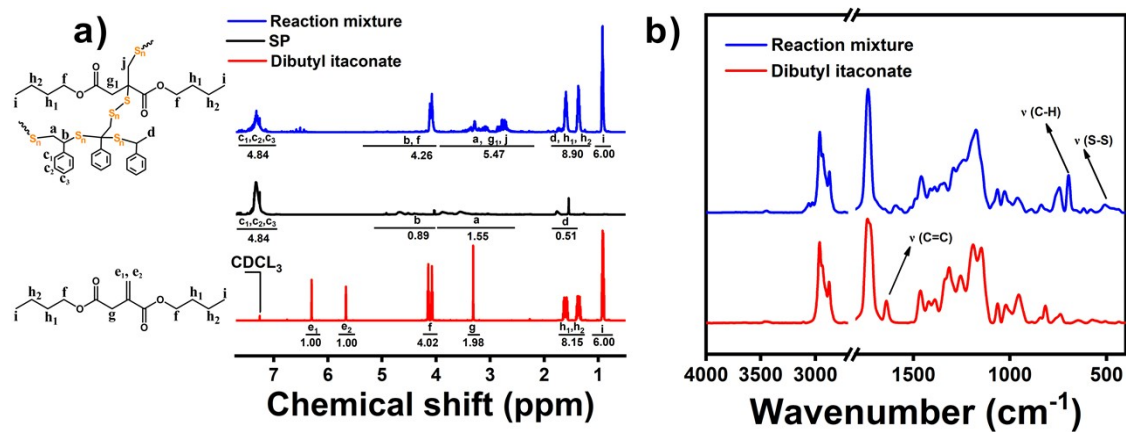
Fig. S6 (a) ^{1}H NMR of the reaction mixture, SP and dibutyl itaconate. (b) FTIR spectra of the reaction mixture and dibutyl itaconate.
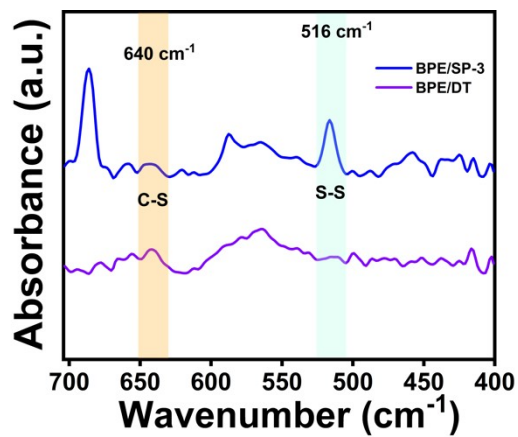

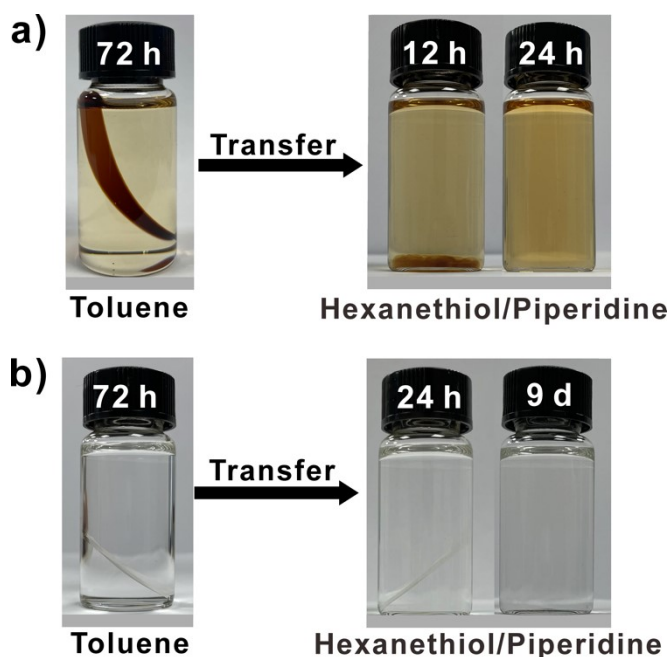**Fig. S7** FTIR spectra of BPE/SP-3 and BPE/DT.

Fig. S8 (a) Photos of BPE/SP-3 in toluene after 72 h, and the swollen BPE/SP-3 in 1-hexanethiol/piperidine solution (1 M) after 12 h and 24 h. (b) Photos of control BPE/DT in toluene after 72 h, and the swollen control sample in 1-hexanethiol/piperidine solution (1 M) after 24 h and 9 days.

XPS analysis was supplemented to investigate the bonding status of sulfur in the crosslinked network. Taking BPE/SP-3 as an example, the high-resolution S 2p XPS spectrum show that the S 2p peaks are composed of two doublets (Fig. S9), representing C-S and S-S bonds at 164.8/163.6 eV and 165.1/163.9 eV, respectively. [2,3] The ratio of S-S to C-S in BPE/SP-3 is 0.60. Accordingly, the S rank in the network is quantitatively calculated to be about 3.2, which is lower than the value of ~4.1 in SP. This is because S-S bonds in SP cleave and react with BPE. It should be noted that a peak at a higher binding energy of 169.6 eV is observed, which may be due to the sulphate species most likely formed by the oxidation of elemental sulfur during the crosslinking process.[7]
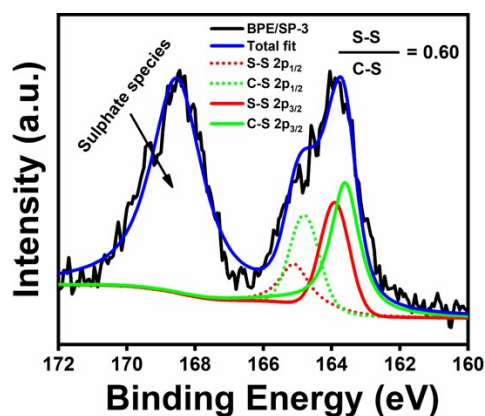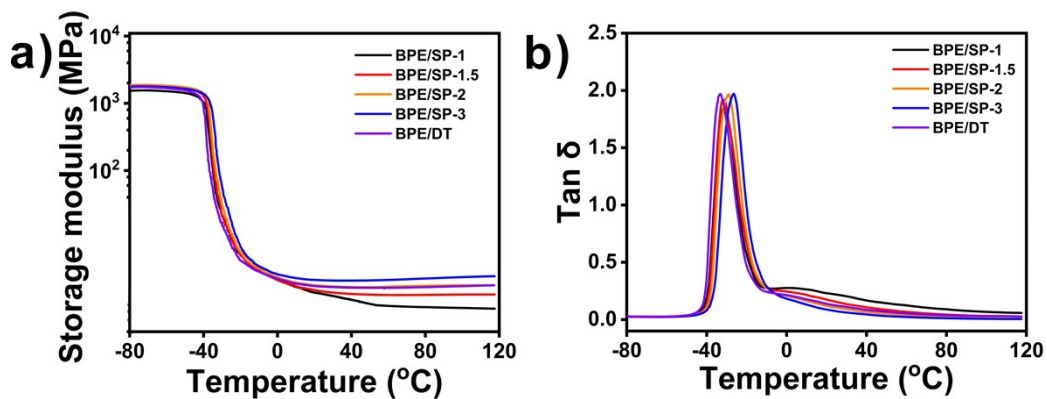

Fig. S9 High-resolution S 2p XPS spectrum of BPE/SP-3.

Fig. S10 (a) Storage modulus versus temperature and (b) tan δ versus temperature for BPE/SP-*x* and BPE/DT.
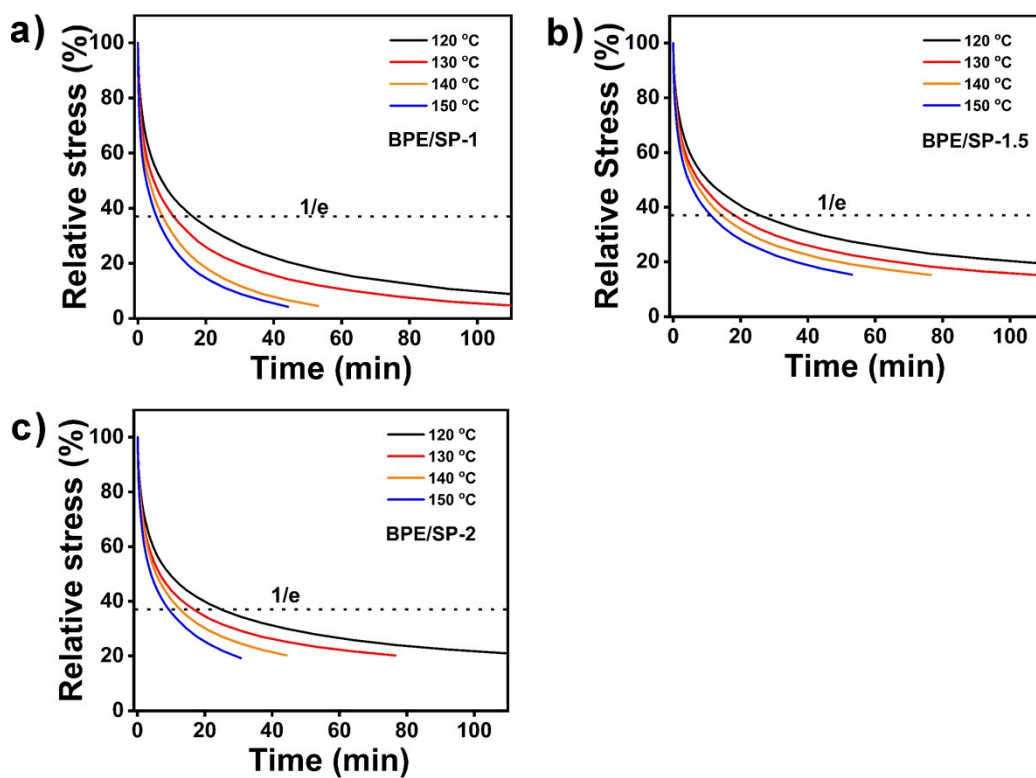

Fig. S11 Stress relaxation curves of (a) BPE/SP-1, (b) BPE/SP-1.5 and (c) BPE/SP-2 at different temperatures.
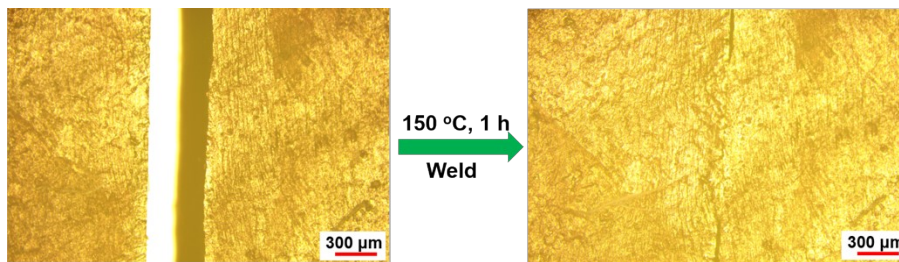
Fig. S12 Optical microscope images showing the joint of the two ends of a strip BPE/SP-3 after being welded at 150 °C for 1 h.
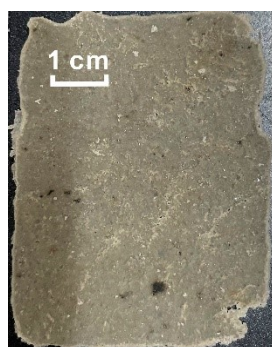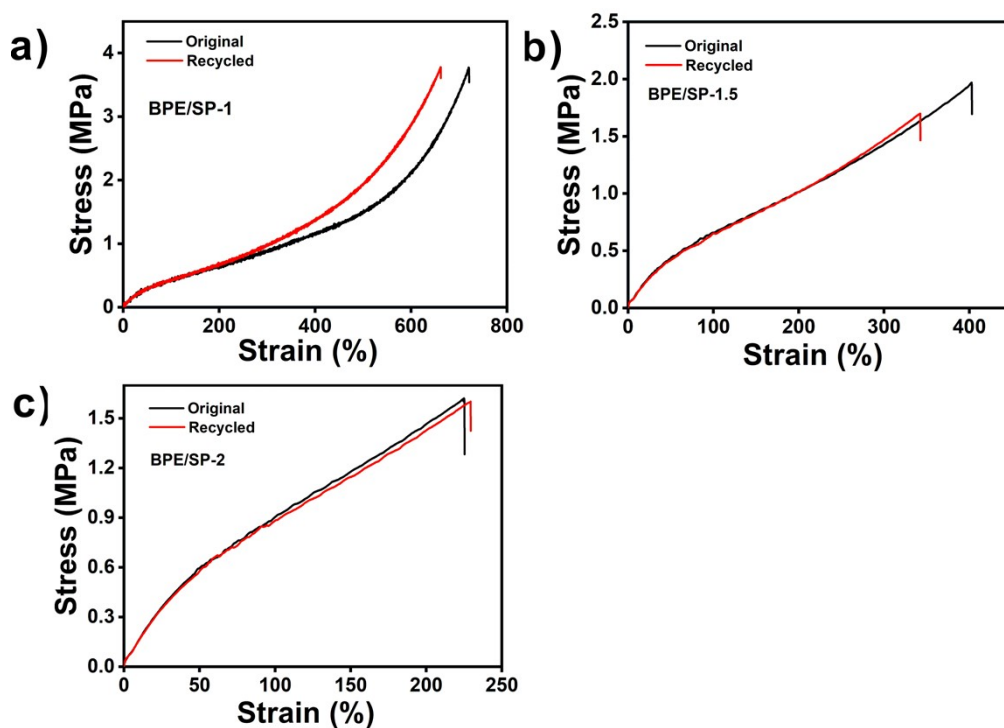

Fig. S13 Photo of the remolded BPE/DT film.

Fig. S14 Comparison on the typical tensile curves of the original and recycled samples. (a) BPE/SP-1, (b) BPE/SP-1.5 and (c) BPE/SP-3.
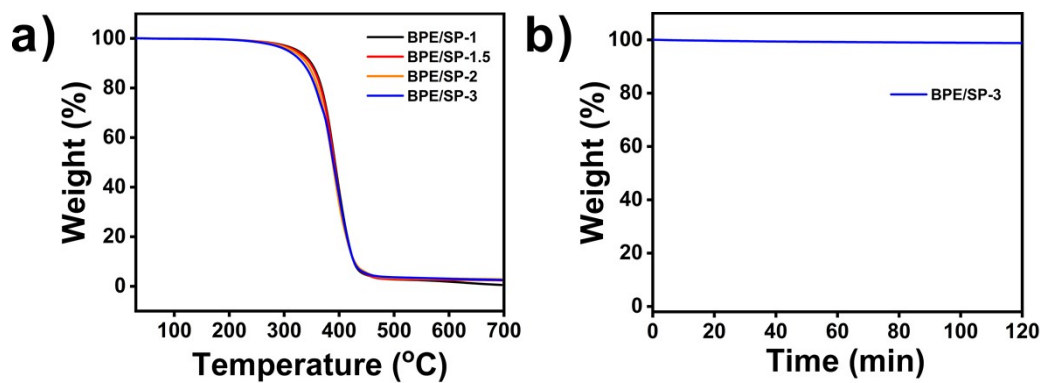
Fig. S15 TGA curves of (a) BPE/SP-*x* and (b) BPE/SP-3 at 180 °C under nitrogen atmosphere.
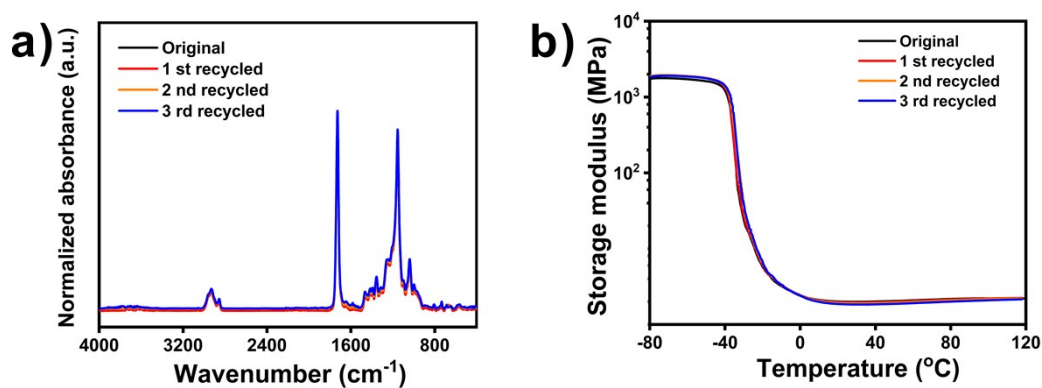

Fig. S16 (a) FTIR spectra and (b) storage modulus versus temperature for original and recycled BPE/SP-3.
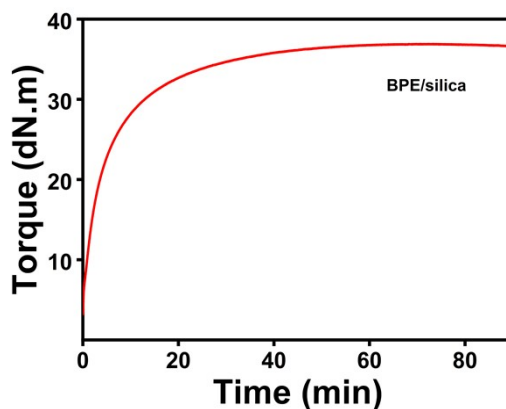

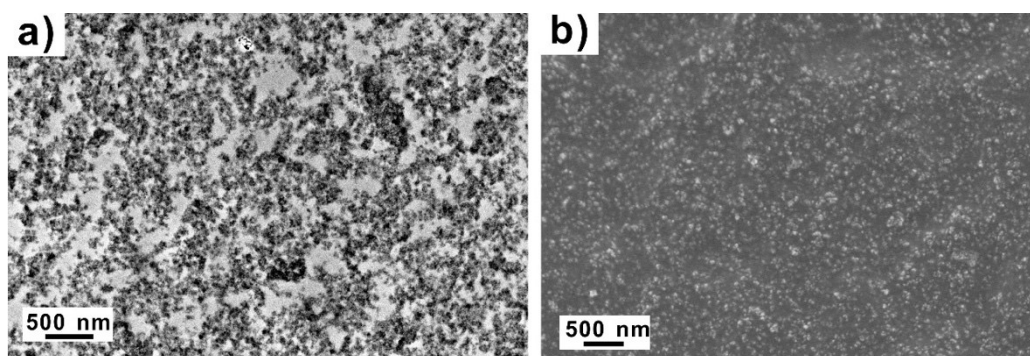**Fig. S17** Evolution of torque during curing at 160 °C.

Fig. S18 (a) TEM image and (b) SEM image of the BPE/silica composite.
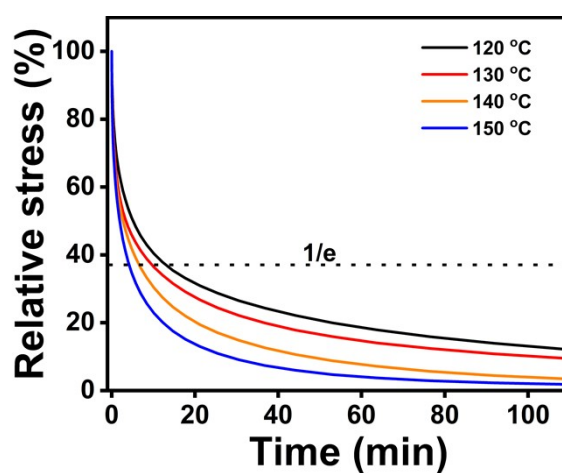

Fig. S19 Stress relaxation curves of the BPE/silica composite at different temperatures.
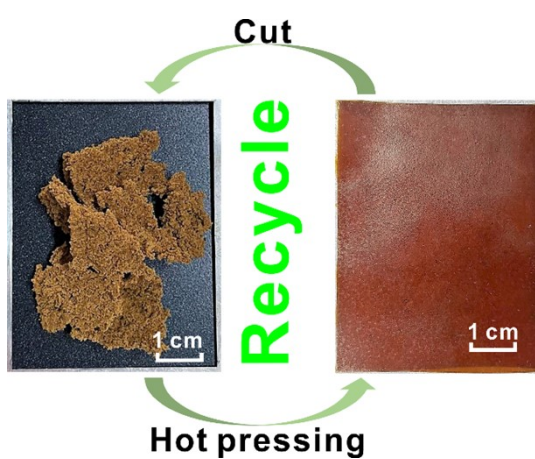

Fig. S20 Photos showing the thermal recycling of the BPE/silica composite.

Table S1 Mechanical properties of BPE/SP-*x*.

Samples	Tensile strength (MPa)	Breaking strain (%)	Tensile modulus (MPa)
BPE/SP-1	3.59±0.30	706±17	0.41±0
BPE/SP-1.5	2.04±0.08	407±14	0.64±0.02
BPE/SP-2	1.65±0.02	229±5	0.90±0
BPE/SP-3	1.24±0.03	116±5	1.11±0.01

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