

Supporting Information

Dual-crosslinking side-chains with asymmetric chain structure: a facile pathway to robust, self-healable and re-dissolvable polysiloxane elastomer for recyclable flexible device

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Experimental

Materials

Octamethyl cyclotetrasiloxane (D₄), diethylenetriamine propylmethyldimethoxysilane (DETAS), hexamethyldisiloxane (MM) and (3-aminopropyl)diethoxymethylsilane (APDS) provided by Jiangxi Chenguang New Materials Co., Ltd. Tetramethylammonium hydroxide pentahydrate (TMAH), 4-formylbenzoic acid (FBA), terephthalaldehyde (TPD), terephthalic acid (TPA), benzaldehyde (BD), benzoic acid (BA) and lithium bromide (LiBr) were purchased from Sigma-Aldrich.

Synthesis of diethylenetriamine-functionalized polydimethylsiloxane (PDETAS)

As shown in **Scheme S1a**, PDETAS with different amine value was synthesized via hydrolysis polycondensation of D₄, DETAS and MM. Taking PDETAS30 as an example, D₄ (100.0 g, 340 mmol), DETAS (11.2 g, 45 mmol), MM (0.11 g, 0.68 mmol), deionized water (1.62 g, 90 mmol) and TMAH (0.22 g, 0.0012 mol) were mixed mechanically under nitrogen at 95 °C for 5 h. After that, the mixture was maintained at 150 °C with a reduced pressure of -0.1 MPa for 1 h to decompose TMAH and remove volatile small molecules. Finally, a clear and yellowish viscous liquid was obtained. FTIR and ¹H NMR spectra of PDETAS were shown in **Figure S1**. Their physical properties were also summarized in **Table S1**.

As for control sample, aminopropyl-functionalized polydimethylsiloxane (PMAS, **Scheme S1b**) with only primary amine was also synthesized by similar process from D₄, APDS and MM.

Fabrication of crosslinked polysiloxane elastomer (PDETAS-FBA)

A series of PDETAS-FBA elastomers were prepared by different PDETAS/FBA ratio in **Table S2**. The pre-dissolved FBA by 30 mL Tetrahydrofuran (THF) was mixed with PDETAS at 25 °C for 10 min. After the obtained viscous liquid was poured into polytetrafluoroethylene (PTFE) mold, the elastomer was dried at 25 °C for 12 h and 100 °C for 2 h to promote the crosslinking.

All the control samples (**Table S3**) were also prepared as the above procedures. PMAS10-FBA-2 was similar to PDETAS10-FBA-2 but PDETAS10 was replaced by PMAS10, which contained asymmetric

chain structure of imine and ionic hydrogen bonds but without dual-crosslinked architecture. PDETAS10-TPD-2, PDETAS10-TPA-2 and PDETAS10-TPA-TPD-2 were also similar to PDETAS10-FBA-2 while the crosslinker FBA was replaced by equimolar TPD or/and TPA, respectively. Regarding to PDETAS10-FBA-2-BA, PDETAS10-FBA-2-BD, PDETAS10-FBA-2-LiBr samples, equimolar BA, BD or LiBr were added into the formula of PDETAS10-FBA-2 to disturb the formation of crosslinking.

Characterization

Variable-temperature infrared spectra were recorded by a Nicolet 8700 spectrophotometer equipped with an external heating cell at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from 4000 to 600 cm^{-1} with a 4 cm^{-1} resolution. NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz NMR spectrometer using CDCl_3 (PDETAS) and THF-*d*8 (PDETAS-FBA). IR spectra were recorded on a Nicolet iS50 spectrometer (Thermo Fisher) by a disc of KBr with a resolution of 4 cm^{-1} from 4000 to 600 cm^{-1} . The amine values of PDETAS were evaluated by chemical titration according to ASTM D2074-07. Their molecular weight (M_n) and polydispersity were evaluated by Waters 1515 gel permeation chromatograph, eluted with THF at 1 mL min^{-1} and polystyrene as standard reference. Dynamic mechanical analysis (DMA) was measured using Metravib DMA-50N with a dynamic displacement of 10^{-5} m and a frequency of 1 Hz , from 30 to $200\text{ }^{\circ}\text{C}$ by $5\text{ }^{\circ}\text{C min}^{-1}$. Stress relaxation was also measured on Metravib DMA-50N using tensile mode with a fixed deformation of 10% at various temperatures. Rheology analyses were recorded on a HAAKE MARS 60 rheometer (Thermo Fisher) with a 20 mm parallel-plate geometry, frequency of 1.0 Hz , strain of 0.5% , and heating rate of $0.2\text{ }^{\circ}\text{C s}^{-1}$. Morphological observation (SEM) and energy dispersive spectroscopy (EDS) analyses were conducted on a field emission scanning electron microscope (Hitachi S-4800). The specimen dimension was 12.5 mm in diameter and 0.5 mm in thickness. The mechanical strength was estimated on a SANS CMT 6000 Universal Tester according to ASTM D412 at $25\text{ }^{\circ}\text{C}$. Type D dumbbell-shaped samples were employed with a cross-head speed of 50 mm min^{-1} . For healing evaluation, the elastomer was cut in half, the fractured surfaces were brought into contact together and heated during different temperature and time. The self-healability was determined by the ratio of tensile

strength of healed samples to that of virgin samples. For reprocessing, the elastomer was cut into small pieces and thermally pressed at 80 °C for 2 h with 10 MPa pressure. The reprocessing ability was also determined by the ratio of tensile strength of recycled sample to that of virgin sample. The elastomer was re-dissolved into THF, and the solution was coated onto a rectangular area of 25 × 20 mm on iron plate (cleaned with acetone in advance). After the solvent was volatilized, it was bonded with another iron plate by a fixture and heated at 100 °C for 2 h. Crosslinking density of polysiloxane elastomer was estimated by the popular equilibrium swelling method.¹ Briefly, about 1.0 g elastomer (W_0) was immersed in toluene at 25 °C for 72 h. The swollen elastomer was removed from toluene, the residual liquid on the sample surface was wiped off with filter paper and weighed (W_1). Finally, the sample was dried at 100 °C by vacuum to constant weight (W_2). The volume fraction of polymer (ϕ) in swollen sample can be obtained by Eq 1:

$$\phi = \frac{W_0/\rho_0}{(W_1 - W_0)/\rho_0 + W_0/\rho_s} \quad (1)$$

where W_0 and W_1 were the weight of virgin sample and swollen sample. ρ_s and ρ_0 were the density of toluene and elastomer, respectively.

The crosslinking density (ν) could be calculated by Eq 2:

$$\nu = - \frac{\ln(1 - \phi) + \phi + \chi\phi^2}{V_0(\phi^{\frac{1}{3}} - \frac{\phi}{2})} \quad (2)$$

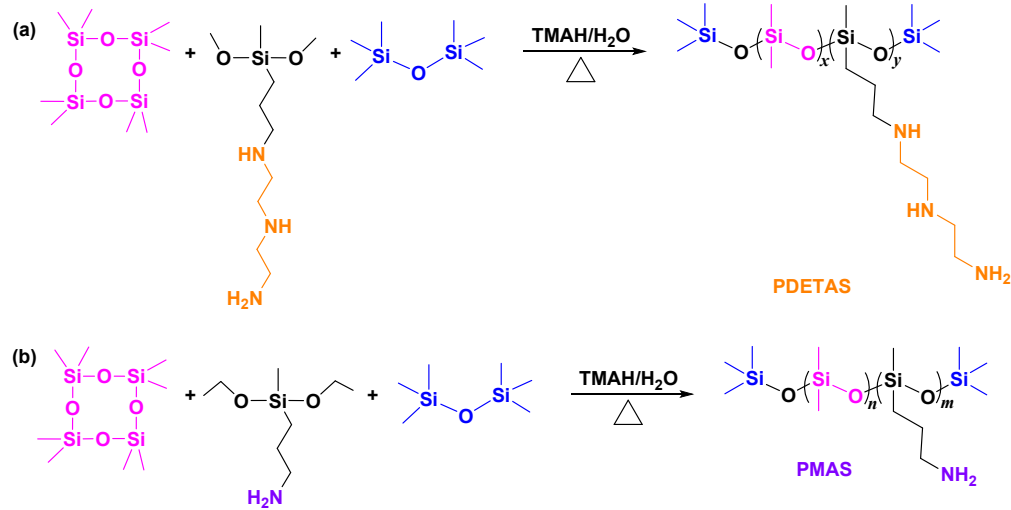
where χ was the Flory-Huggins interaction parameter between polysiloxane elastomer and toluene (0.465).²⁻⁶ V_0 was the molar volume of toluene (105.7 cm³ mol⁻¹).

The cavity radius in different elastomer was investigated on a positron annihilation lifetime spectrometer (PALS, ORTEC 0107A) with ²²Na as the radiation source. The quantitative relation between orthopositronium (o-Ps) lifetimes (τ_3) and cavity radius of free volume (R) was described as Eq 3:⁷

$$\tau_3 = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R_0} \right) \right]^{-1} \quad (3)$$

where $R_0 = R + R_\delta$. R_δ is a semi-empirical constant, 1.656×10^{-1} nm. Assuming that the free volume hole is spherical, its free volume hole size (V_f) could be calculated by Eq 4:

$$V_f = \frac{4}{3} \pi R^3 \quad (4)$$



Scheme S1. Synthesis of PDETAS and PMAS.

Table S1 Raw materials and physical properties of different PDETAS and PMAS.

Samples	D ₄ [mmol]	DETAS or APDS [mmol]	$n_{(D)}/n_{(A)}$	M_n [g mol ⁻¹]	PDI	Amine value [mmol g ⁻¹]
PDETAS30	340	45.4	30	21697 ± 1532	1.38 ± 0.09	1.12 ± 0.11
PDETAS15	340	90.7	15	9973 ± 848	1.53 ± 0.05	2.18 ± 0.15
PDETAS10	340	136	10	7238 ± 486	1.36 ± 0.12	3.04 ± 0.17
PMAS10	340	136	10	8374 ± 683	1.47 ± 0.15	1.23 ± 0.08
PMAS2.5	340	544	2.5	7359 ± 722	1.42 ± 0.09	3.11 ± 0.13

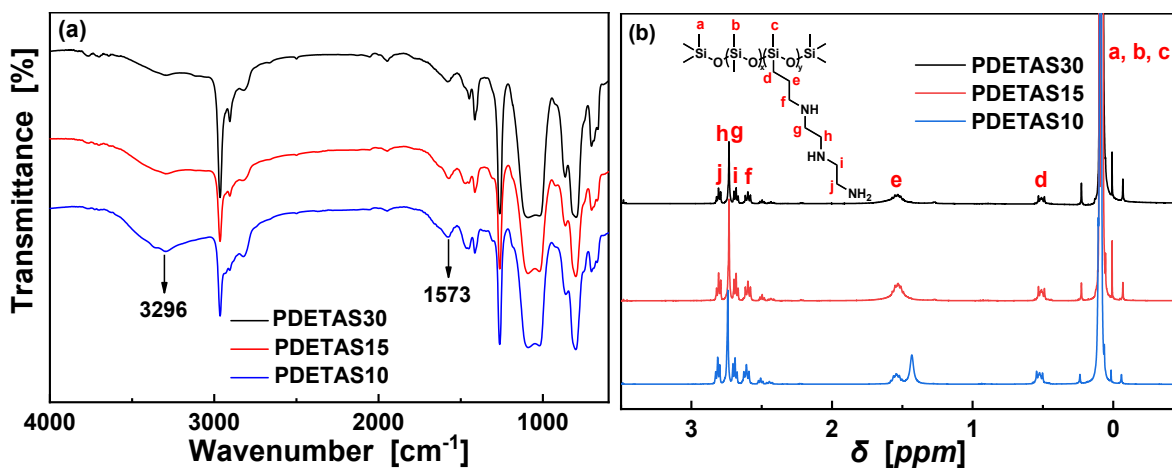


Figure S1. (a) FTIR and (b) ^1H NMR of the synthesized PDETAS.

The peaks at 3296 and 1573 cm^{-1} were attributed to the N-H stretching and bending vibration of primary and secondary amine groups. The bands at 2962 and 1261 cm^{-1} belonged to the C-H stretching vibration of alkyl groups and the symmetric deformation of Si-CH₃, respectively. The dual peaks at 1100 and 1023 cm^{-1} ascribed to the Si-O-Si stretching vibration. ^1H NMR spectra in Figure S1b indicated that the strong peak at 0.02 *ppm* represented the protons of methyl groups. The peaks at 0.45, 1.47 and 2.5 ~ 2.77 *ppm* were the protons of methylene in the side diethylenetriamine propyl groups.

Table S2 Formulas of different PDETAS-FBA elastomers.

Samples	PDETAS [g]	FBA [g]	$n(\text{NH}\&\text{NH}_2)/n(\text{FBA})$
PDETAS30-FBA-1	10	1.26	1.33
PDETAS30-FBA-2	10	0.84	2.00
PDETAS30-FBA-4	10	0.42	4.00
PDETAS15-FBA-1	10	2.46	1.33
PDETAS15-FBA-2	10	1.64	2.00
PDETAS15-FBA-4	10	0.82	4.00
PDETAS10-FBA-1	10	3.42	1.33
PDETAS10-FBA-2	10	2.28	2.00
PDETAS10-FBA-4	10	1.14	4.00

Table S3 Formulas of control elastomers.

Samples	PDETAS [g]	PMAS [g]	FBA [g]	TPA [g]	TPD [g]
PMAS10-FBA-2	0	10	0.92	0	0
PMAS2.5-FBA-2	0	10	2.33	0	0
PDETAS10-TPA-2	10	0	0	2.53	0
PDETAS10-TPD-2	10	0	0	0	1.36
PDETAS10-TPA-TPD-2	10	0	0	1.26	1.02
PDETAS10-FBA-0.76	10	0	0.76	0	0

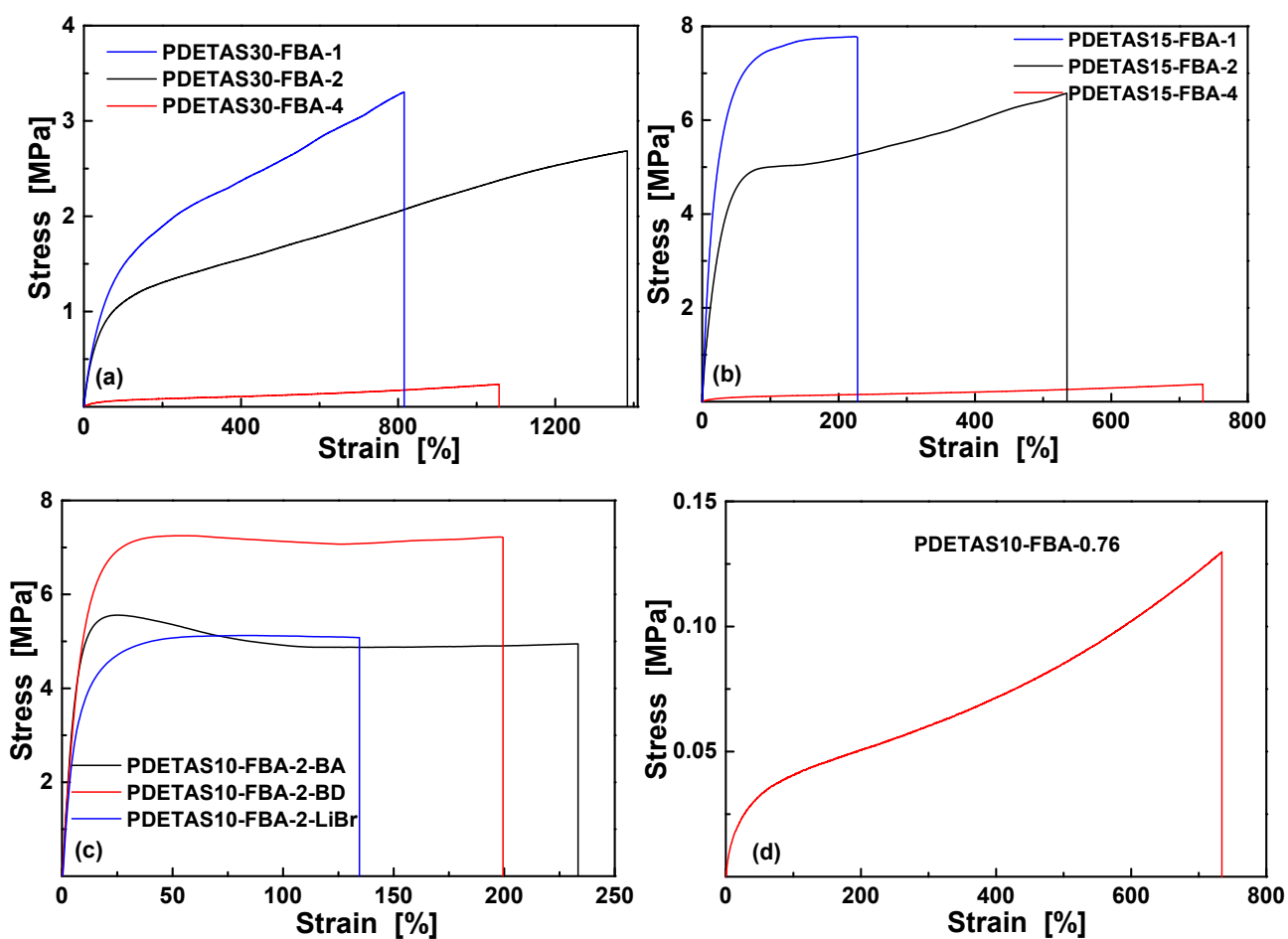


Figure S2. Typical stress-strain curves of polysiloxane elastomers (a) PDETAS30-FBA, (b) PDETAS15-FBA, (c) PDETAS10-FBA-2 with different competitive reagents, and (d) PDETAS10-FBA-0.76.

Table S4 Mechanical properties and crosslinking density of PDETAS-FBA-2 and control samples.

Samples	Tensile strength [MPa]	Elongation at break [%]	Young's modulus [MPa]	Toughness ^{a)} [MJ m ⁻³]	$\nu \times 10^5$ [mol cm ⁻³]
PDETAS30-FBA-2	2.60 ± 0.08	1380 ± 35	2.32 ± 0.16	26.03 ± 1.95	7.75 ± 0.18
PDETAS15-FBA-2	6.45 ± 0.12	539 ± 26	19.72 ± 1.17	28.58 ± 1.77	48.89 ± 1.55
PDETAS10-FBA-2	12.02 ± 0.11	230 ± 13	95.17 ± 9.81	25.63 ± 1.16	129.08 ± 6.33
PDETAS10-TPA-2	1.73 ± 0.08	15 ± 3	17.54 ± 0.95	0.15 ± 0.03	134.48 ± 7.68
PDETAS10-TPD-2	2.78 ± 0.15	22 ± 5	34.22 ± 2.54	0.43 ± 0.12	117.35 ± 4.83
PDETAS10-TPA-TPD-2	2.08 ± 0.06	87 ± 8	4.65 ± 0.23	1.09 ± 0.19	122.16 ± 4.57
PMAS10-FBA-2	0.53 ± 0.05	214 ± 21	0.49 ± 0.05	0.66 ± 0.14	96.79 ± 2.43
PMAS2.5-FBA-2	5.23 ± 0.19	261 ± 18	47.15 ± 3.21	11.41 ± 0.82	169.92 ± 6.23

^{a)} The toughness was the integral area of stress-strain curve.

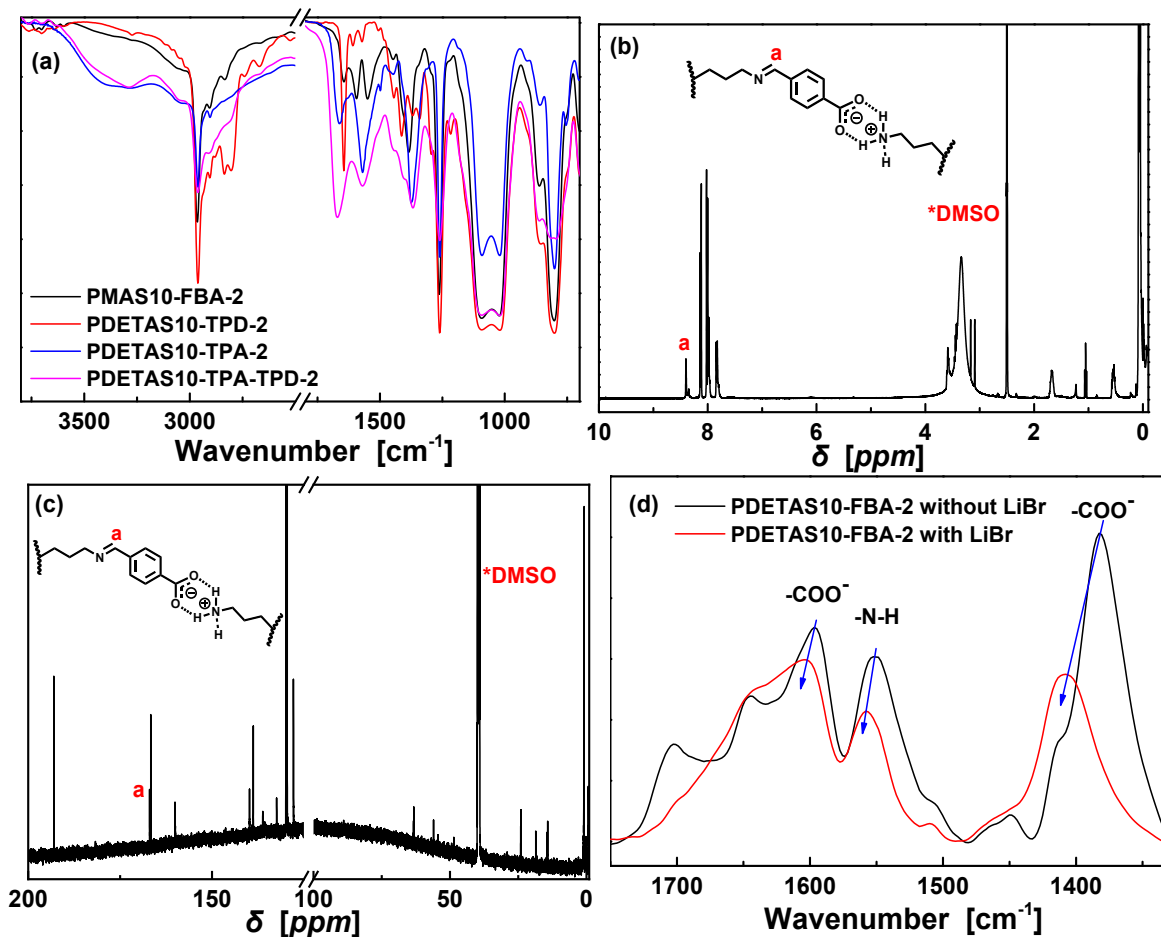


Figure S3. (a) IR spectra of four control samples. (b) ¹H NMR and ¹³C NMR of PMAS10-FBA-2. (d) ATR-IR spectra of PDETAS10-FBA-2 with or without LiBr.

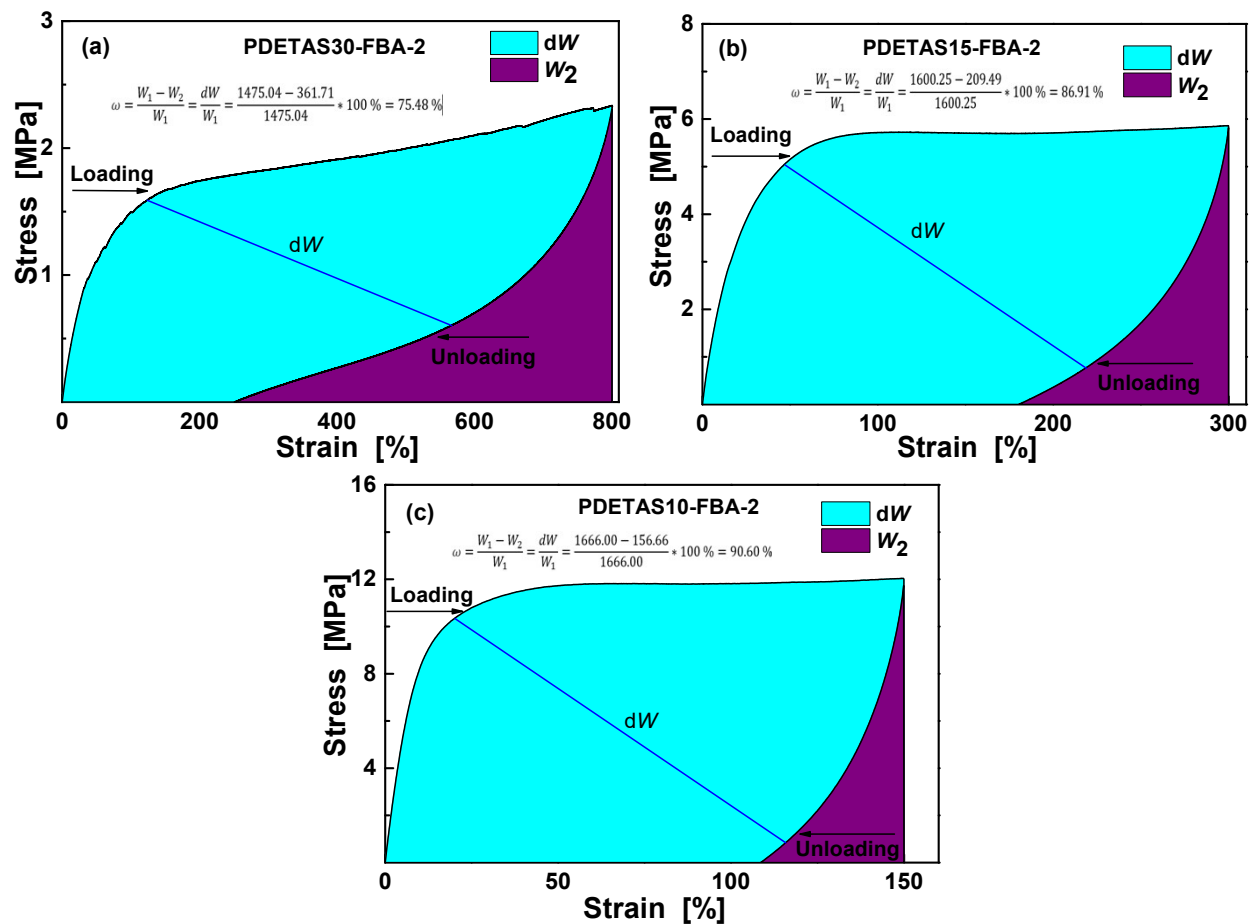
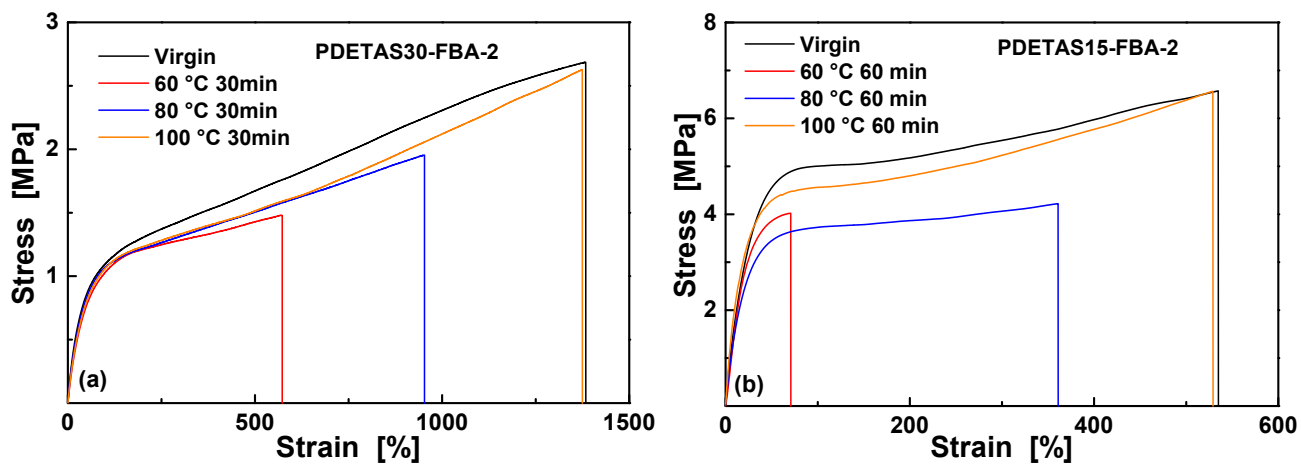


Figure S4. Energy dissipation efficiency of PDETAS-FBA-2 samples.



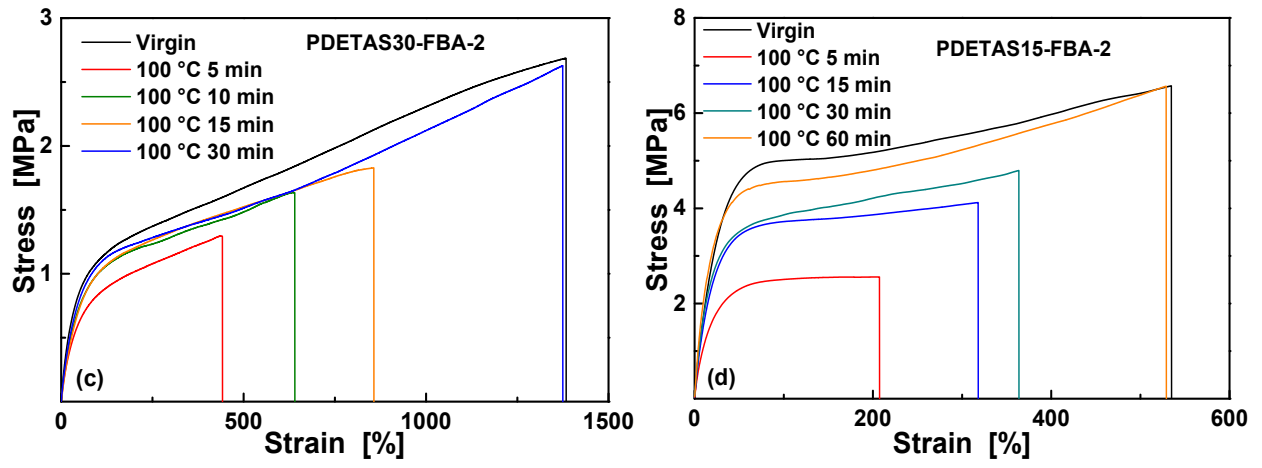


Figure S5. Stress-strain curves of virgin and heated PDETAS-FBA-2 samples (a-b) at different self-heating temperatures and (c-d) for different self-heating time.

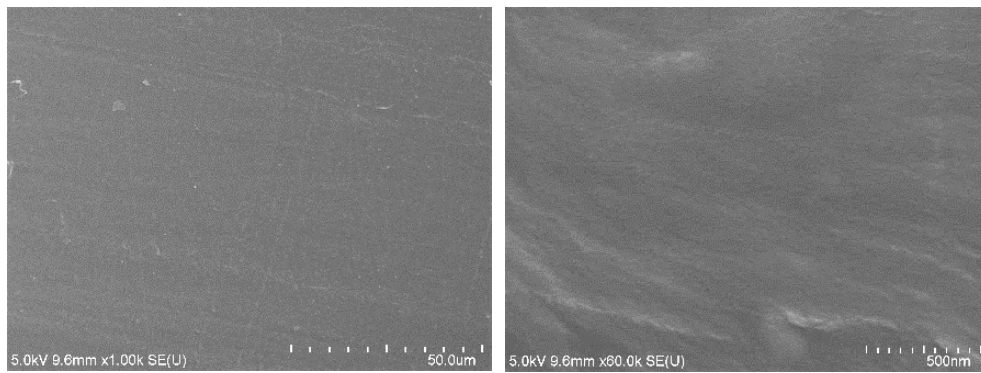


Figure S6. SEM images of reprocessed PDETAS10-FBA-2 at different magnifications.

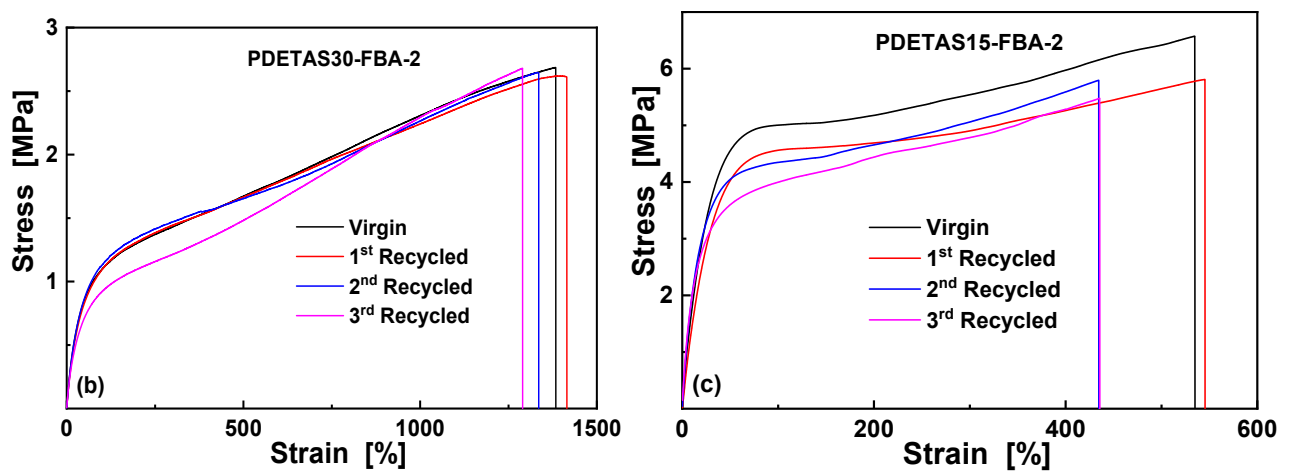


Figure S7. Tensile stress-strain curves of virgin and repeatedly reprocessed PDETAS-FBA-2 samples.

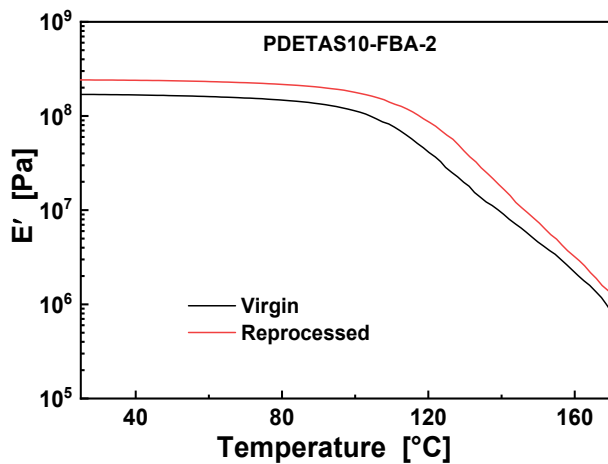


Figure S8. E' of the virgin and reprocessed PDETAS10-FBA-2 samples.

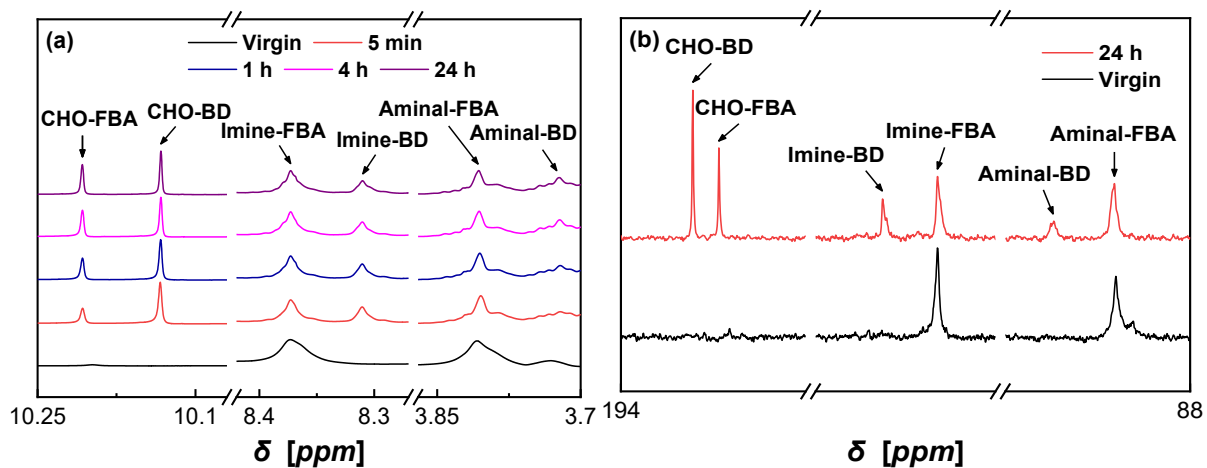
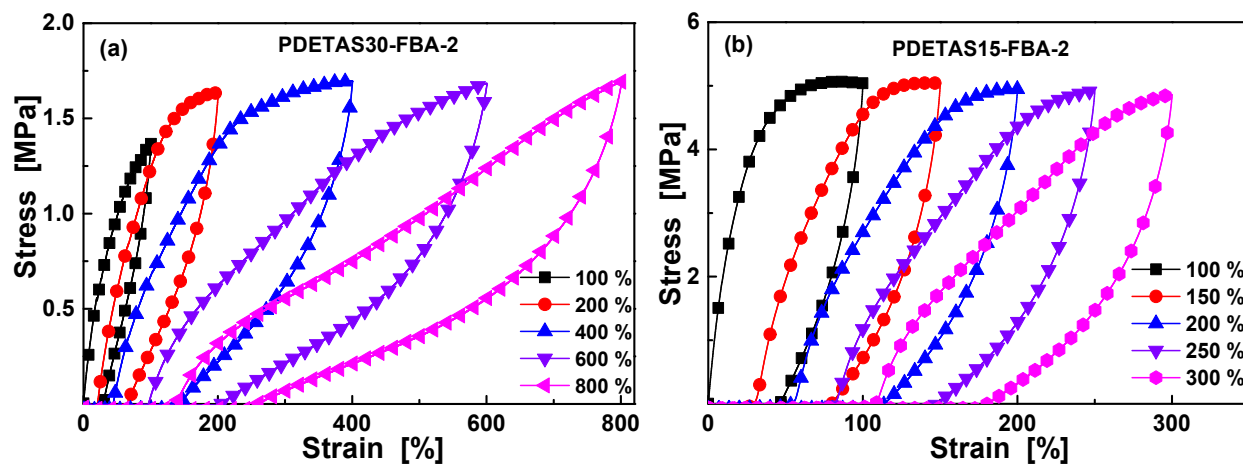


Figure S9. (a) ^1H NMR and (b) ^{13}C NMR spectra of PDETAS10-FBA-2 before and after re-adding benzaldehyde (BD).



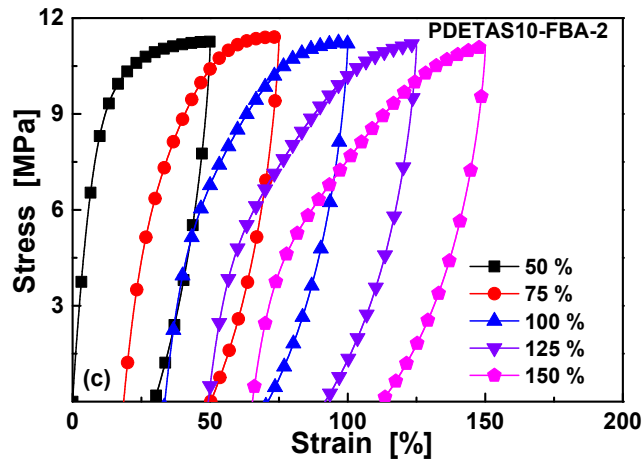


Figure S10. Successive loading-unloading curves of PDETAS-FBA-2 samples under different strains.

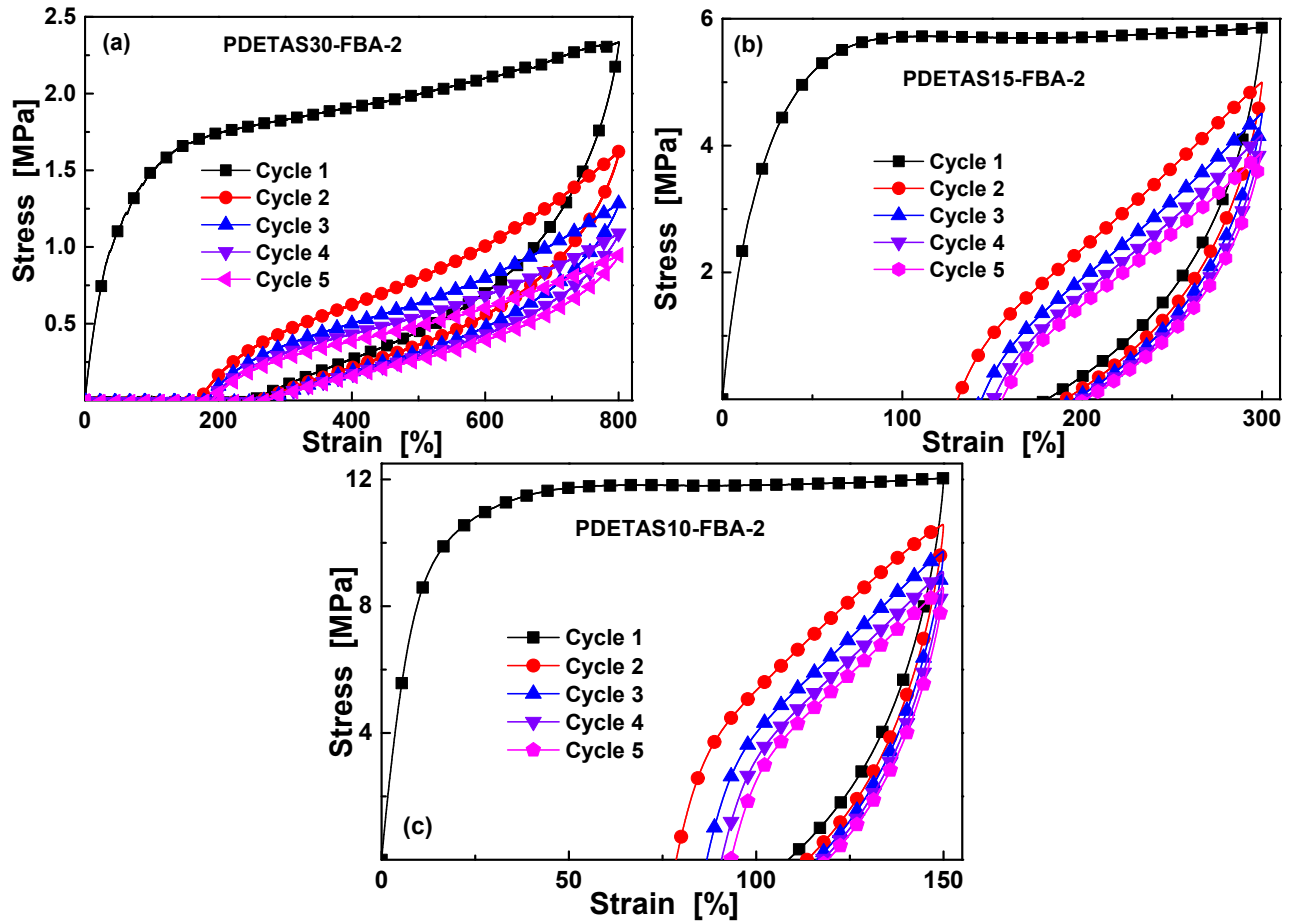


Figure S11. Successive loading-unloading curves of PDETAS-FBA-2 samples at a fixed strain.

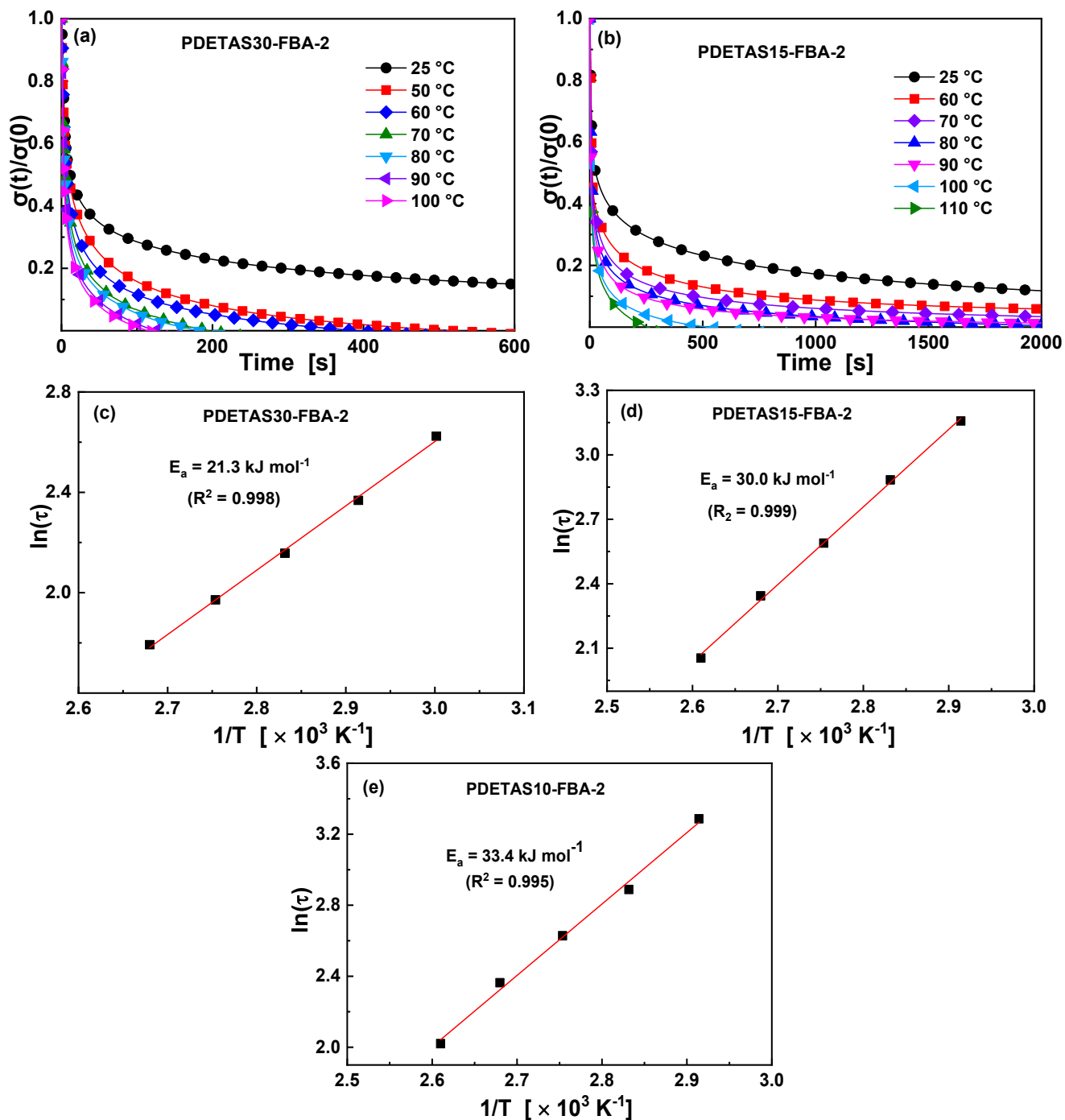


Figure S12. (a, b) Normalized stress-relaxation curves of PDETAS30-FBA-2 and PDETAS15-FBA-2 at diverse temperatures, (c-e) the linear fitting between relaxation time (τ) and reciprocal temperature according to the Arrhenius equation.

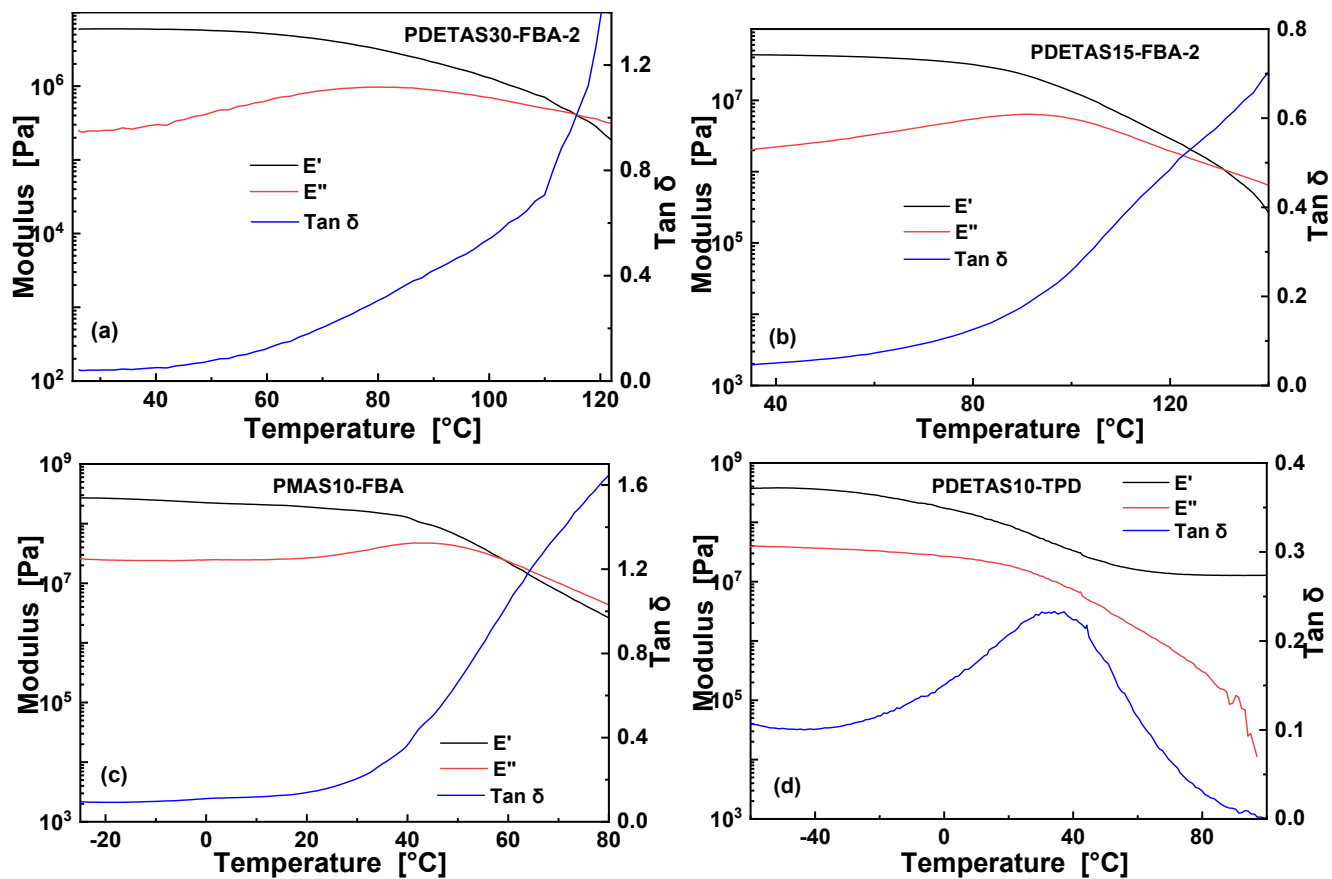


Figure S13. DMA curves of (a) PDETAS30-FBA-2, (b) PDETAS15-FBA-2, (c) PMAS10-FBA-2 and (d) PDETAS10-TPD-2.

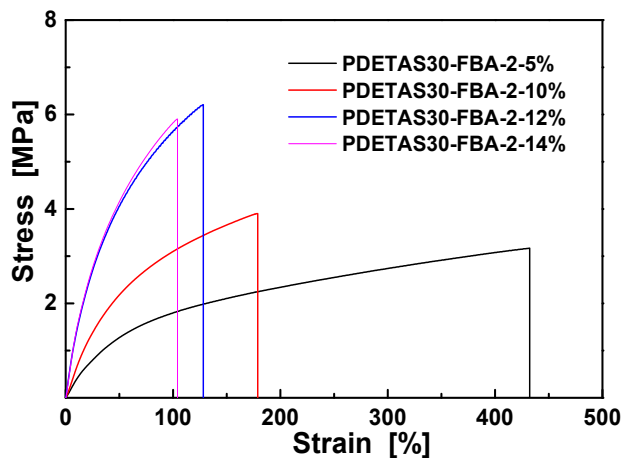


Figure S14. Tensile stress-strain curves of PDETAS30-FBA-2 composited with different contents of MWCNTs.

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