Supplementary information

Dissociate Transfer Exchange of Tandem Dynamic Bonds Enables Covalent Adaptable Networks Fast Reprocessability & High Performance

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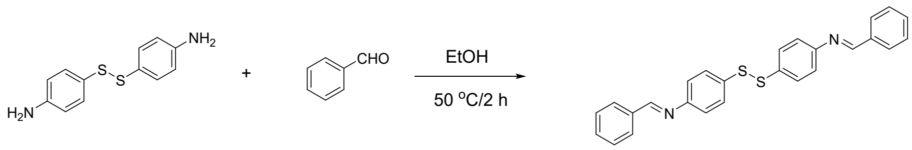
Synthesis of disulfanediylbis(4,1-phenylene)bis(1-phenylmethanimine) (DSBP)

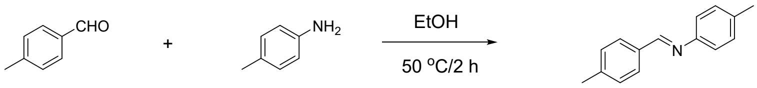
4.96 g (0.02 mol) of 4,4'-dithiodianiline and 4.24 g (0.04 mol) of benzaldehyde were dissolved in 200 mL of EtOH, and poured into a 500-mL flask equipped with a magnetic stirrer. The mixture reacted at 50 °C for 2 h, and a large amount of light-yellow powder disulfanediylbis(4,1-phenylene)bis(1-phenylmethanimine) (DSBP, 6.98 g, yield: 82.2%) was obtained by suction and being dried in a vacuum oven at 80 °C for 4 h.



Scheme S1 Synthetic route of DSBP.

Synthesis of di-*p*-tolylmethanimine (DTMI)

2.40 g (0.02 mol) of *p*-tolualdehyde and 2.14 g (0.02 mol) of *p*-toluidine were dissolved in 100 mL EtOH, and poured into a 250-mL flask equipped with a magnetic stirrer. The mixture reacted at 50 °C for 2 h, and yellow solution was obtained. Then rotary steaming the solution to about 20 mL at *R.T.*, a large amount of transparent crystal di-*p*-tolylmethanimine (DTMI, 3.28 g, yield: 78.5%) was obtained by suction and being dried in a vacuum oven at 80 °C for 4 h.



Scheme S2 Synthetic route of DTMI.

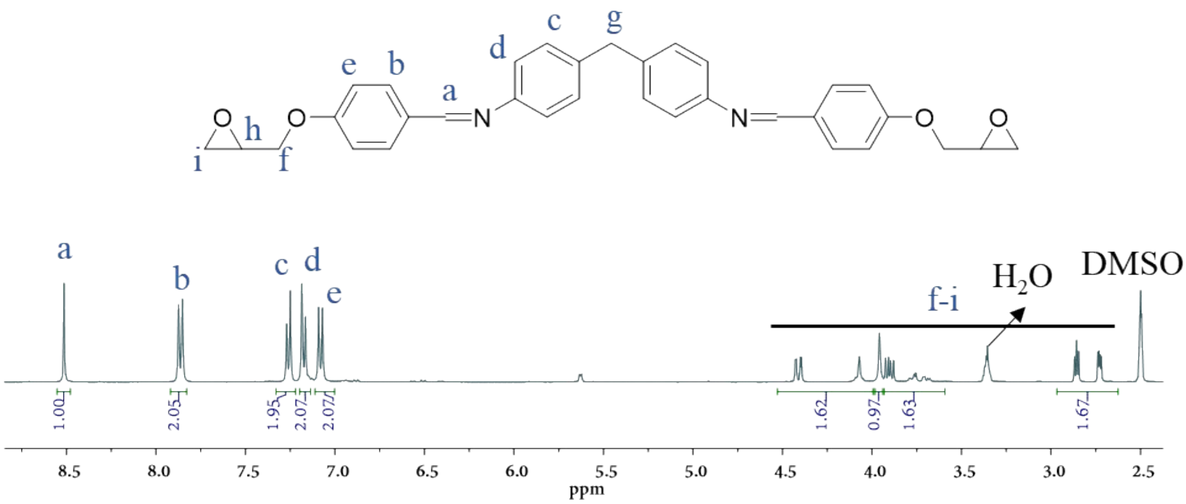


Fig. S1 ^{1}H NMR spectrum of DDMEP.

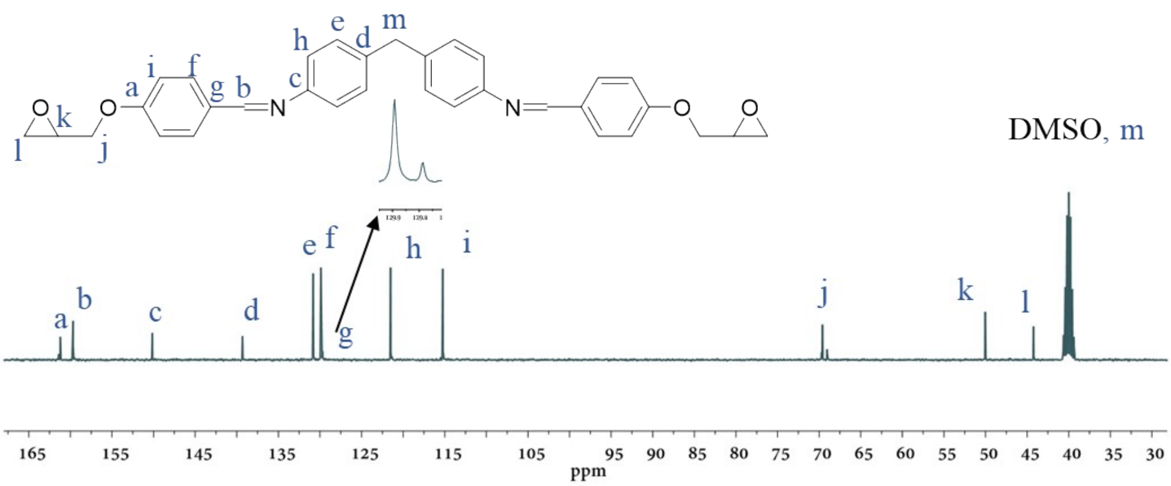


Fig. S2 ^{13}C NMR spectrum of DDMEP.

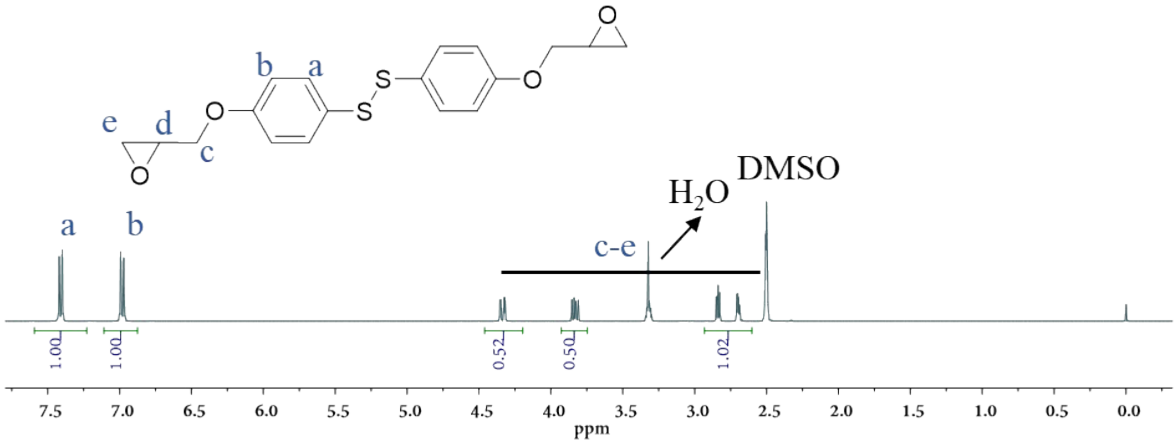


Fig. S3 ^{1}H NMR spectrum of SEP.

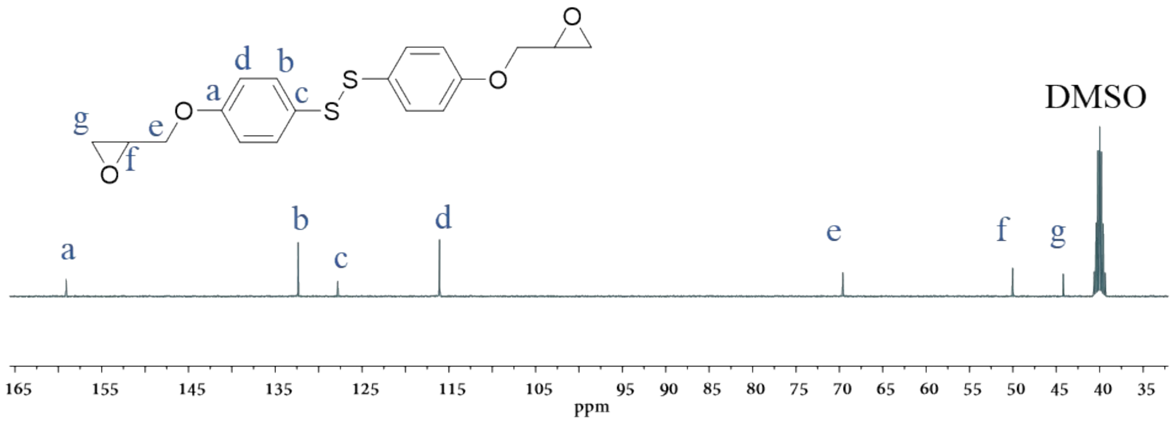


Fig. S4 ^{13}C NMR spectrum of SEP.

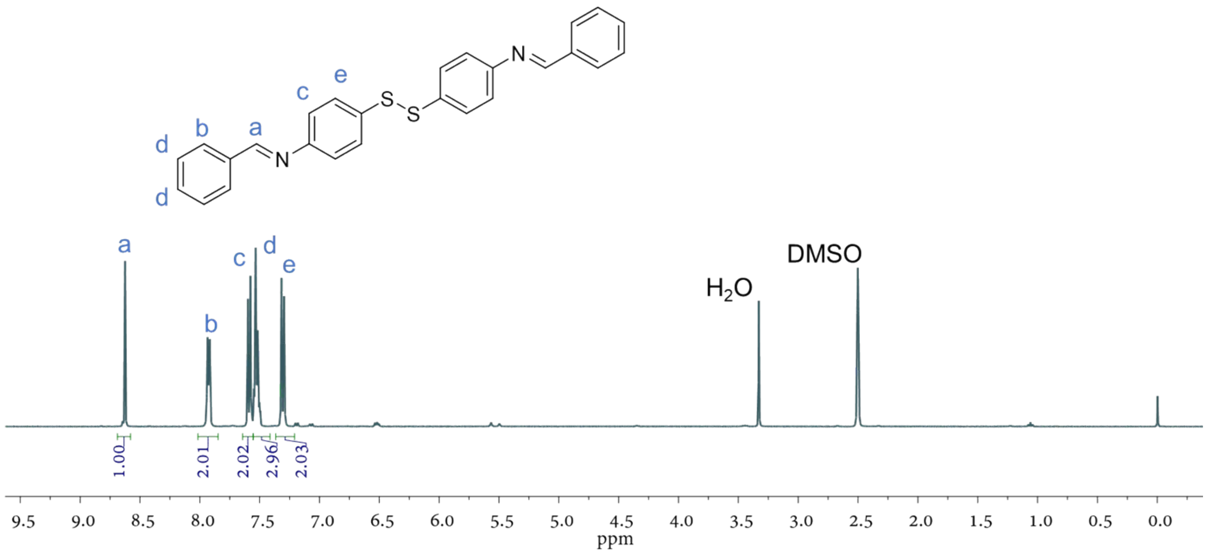


Fig. S5 ^{1}H NMR spectrum of DSBP.

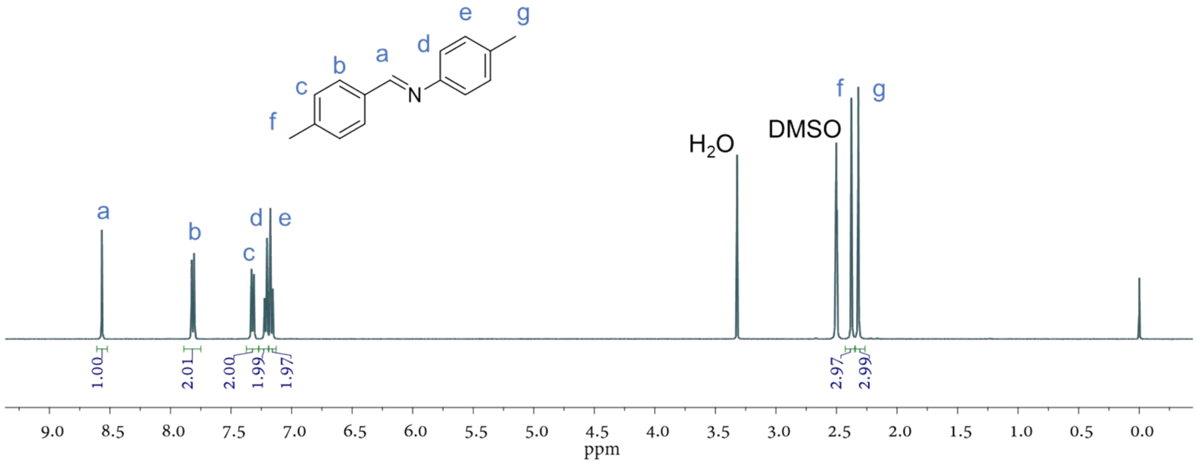


Fig. S6 ^{1}H NMR spectrum of DTMI.

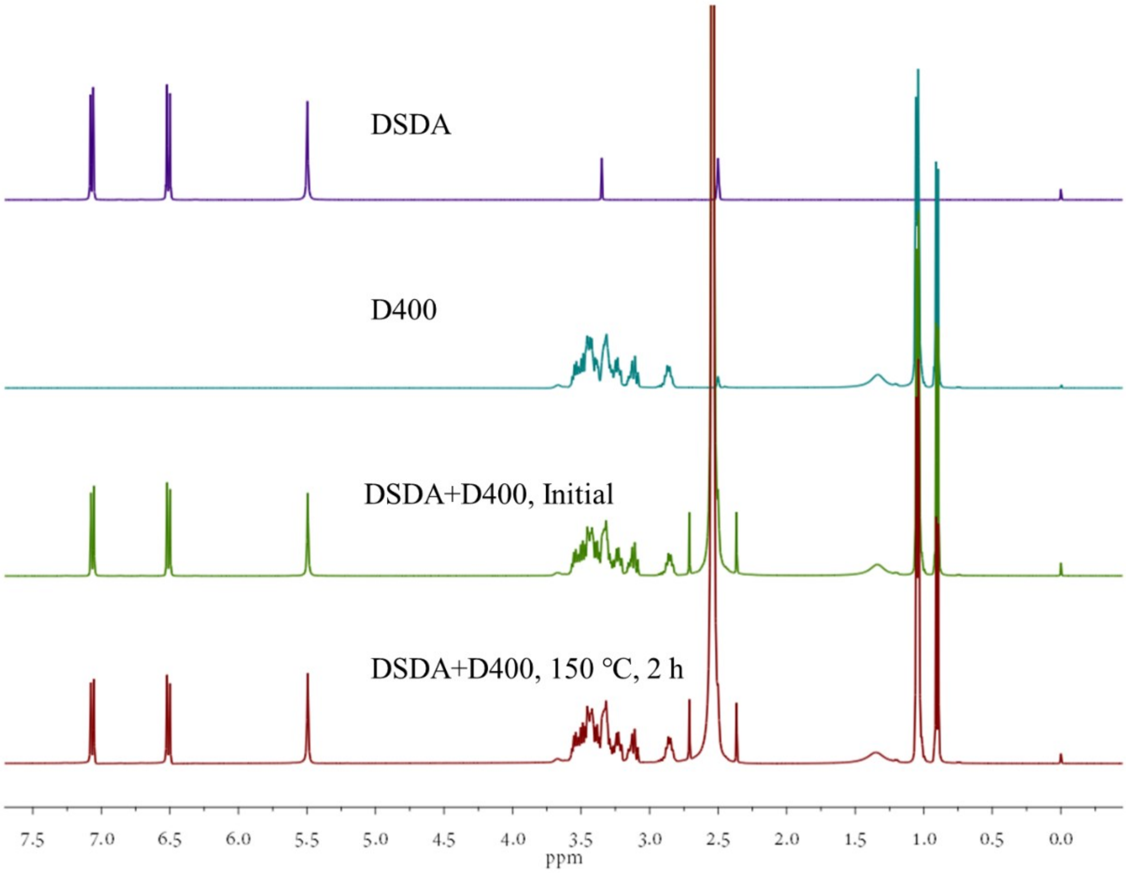


Fig. S7 ^{1}H NMR spectra of DSDA, D400 and their mixture before and after heating at 150 °C for 2 h.

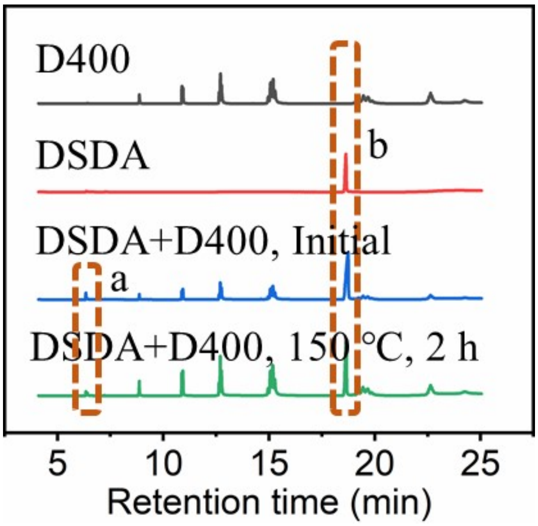


Fig. S8 GC spectra of D400, DSDA and their mixture before and after heating at 150 °C for 2 h.

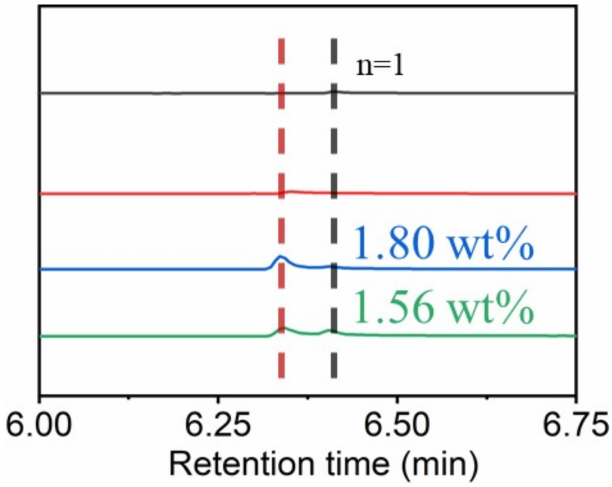


Fig. S9 Enlarged spectra of Fig. S8 at the retention time between 6-6.75 min.

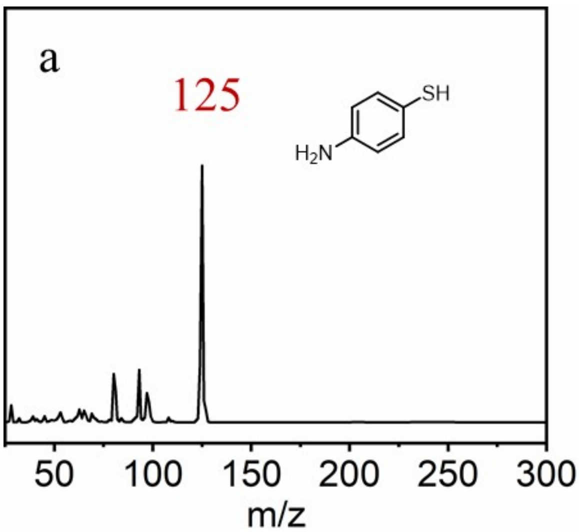


Fig. S10 MS spectrum of compound a in Fig. S8.

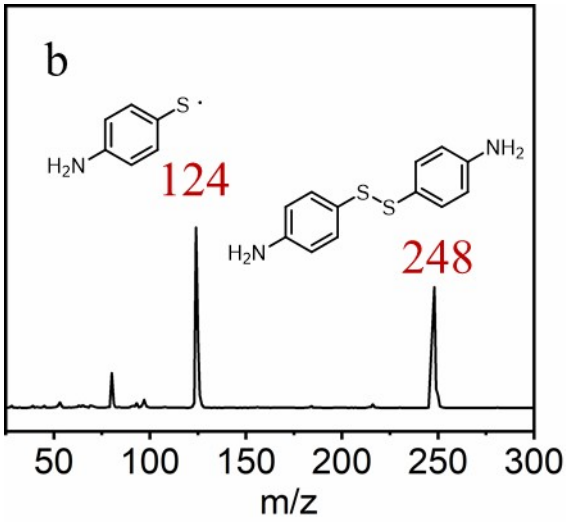


Fig. S11 MS spectrum of compound b in Fig. S8.

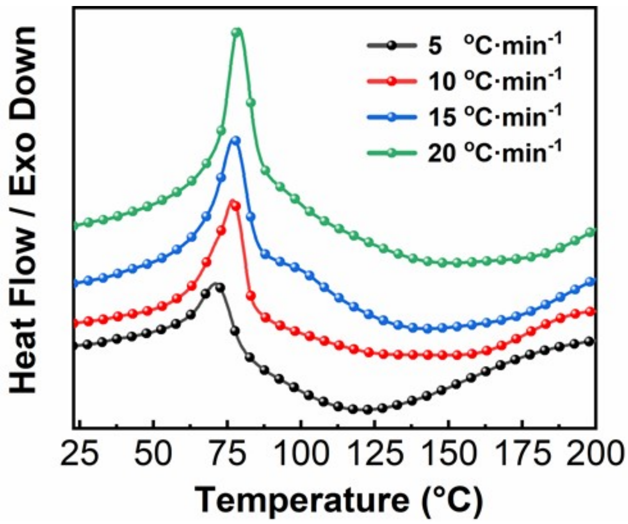


Fig. S12 DSC curves of the SEP-D400 system at different heating rates.

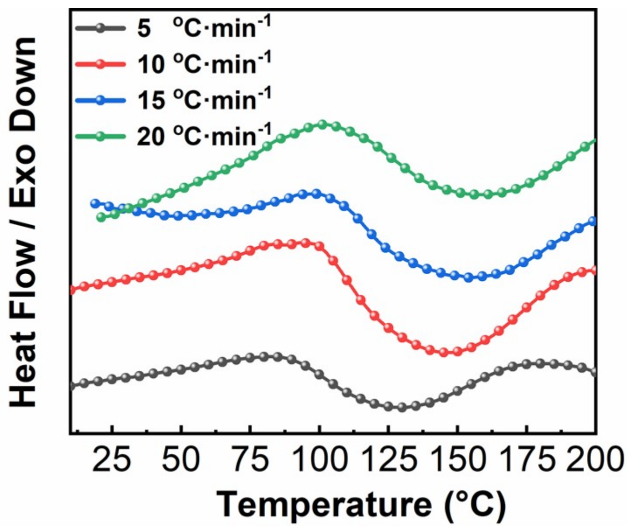


Fig. S13 DSC curves of the DDMEP-D400 system at different heating rates.

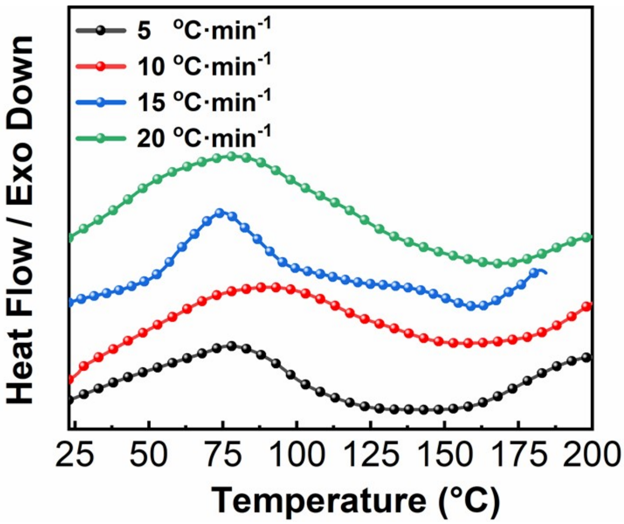


Fig. S14 DSC curves of the DSEP-D400 system at different heating rates.

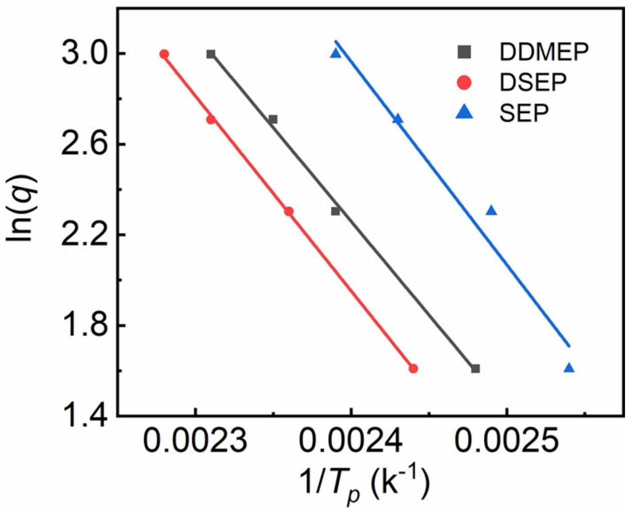


Fig. S15 Linear plots of −ln (q) versus 1/T_p based on Ozawa's theory.

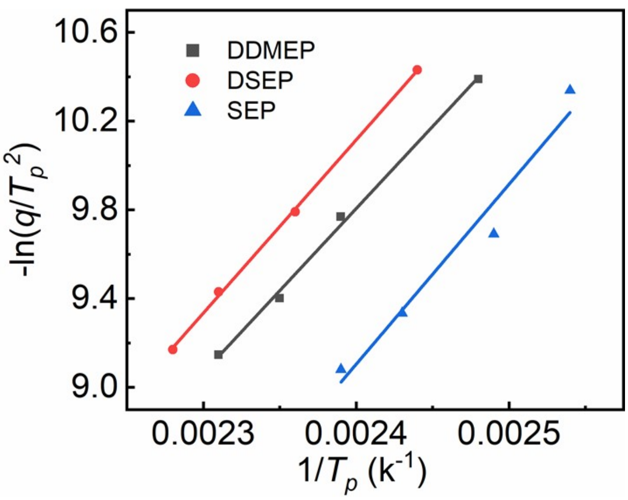


Fig. S16 Linear plots of −ln (q/T_p^2) versus 1/T_p based on Kissinger's equation.

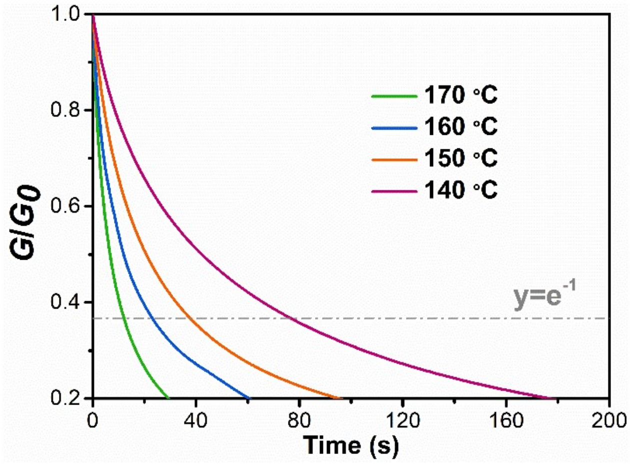


Fig. S17 Stress relaxation curves of DSEP-D400 at different temperatures.

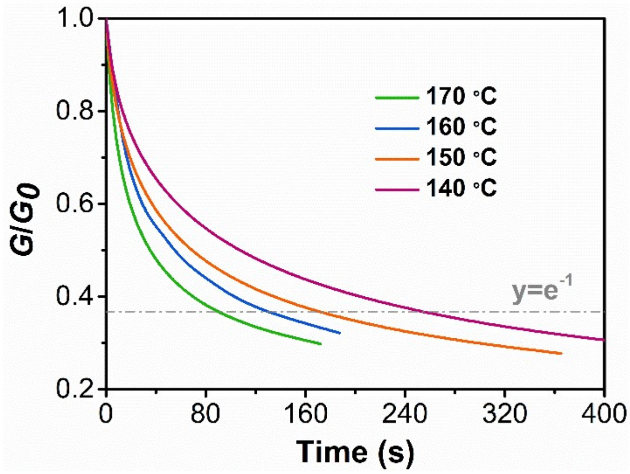


Fig. S18 Stress relaxation curves of DDMEP-D400 at different temperatures.

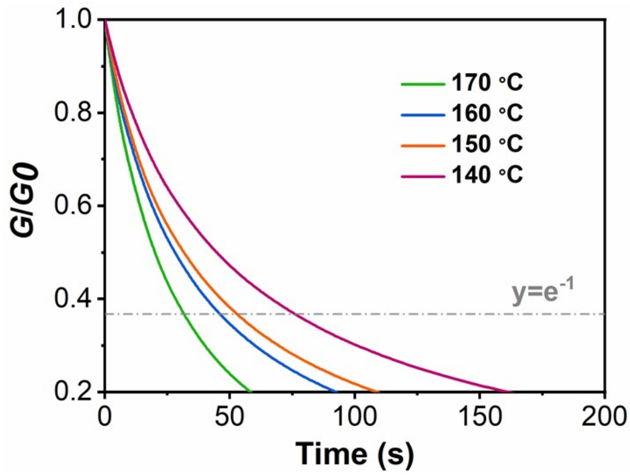


Fig. S19 Stress relaxation curves of DDMEP-SEP-D400 at different temperatures.

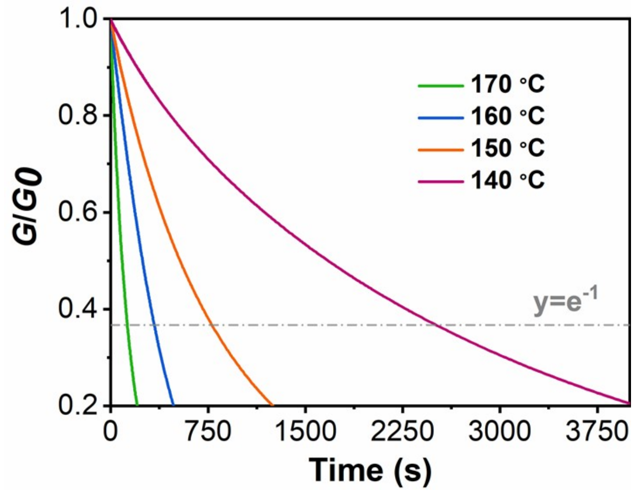


Fig. S20 Stress relaxation curves of SEP-D400 at different temperatures.

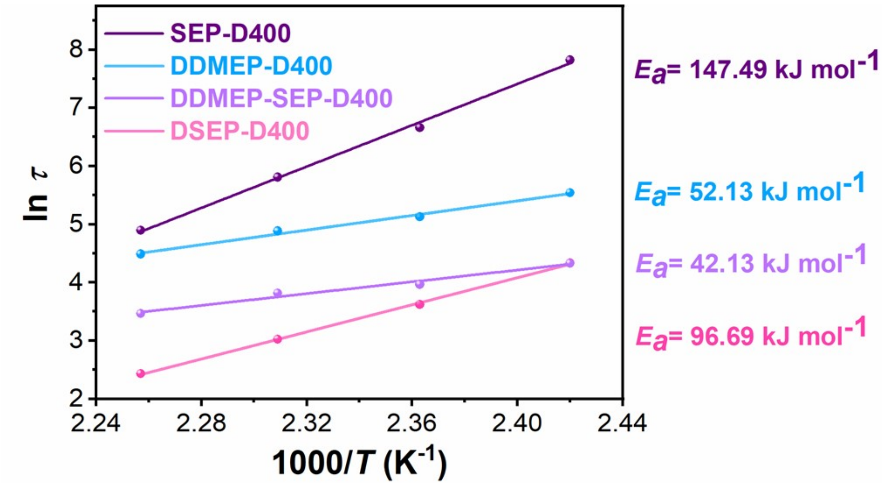


Fig. S21 The fitted curves between ln (τ^*) and 1000/T, and the calculated E_as of the CANs.

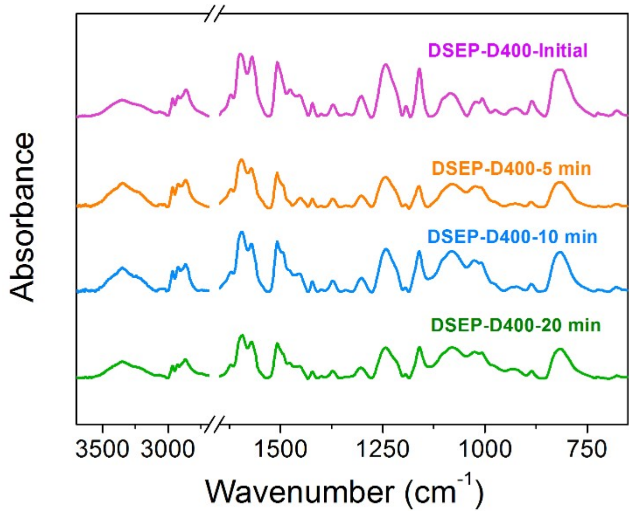


Fig. S22 FTIR spectra of DSEP-D400 after reprocessing by hot press at 160 °C, 10 MPa for different times.

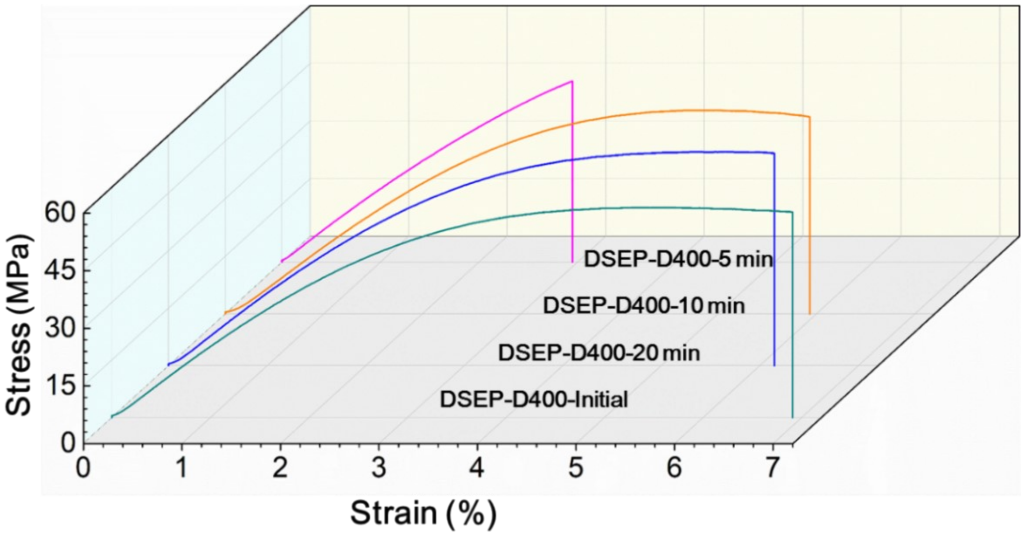


Fig. S23 Representative tensile stress-strain curves of DSEP-D400 after reprocessing by hot press at 160 °C, 10 MPa for different times.

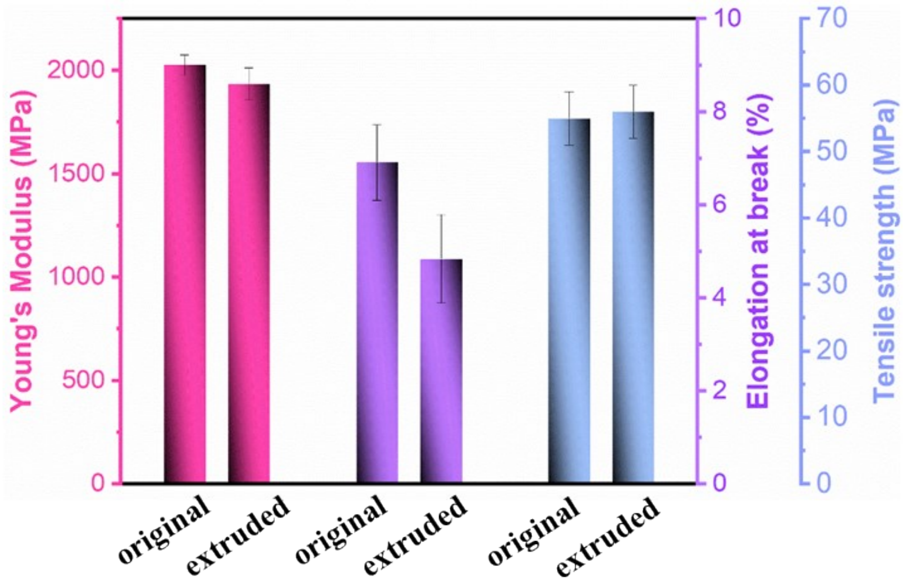


Fig. S24 Young’s modulus, elongation at break and tensile strength of the original and extruded DSEP-D400.

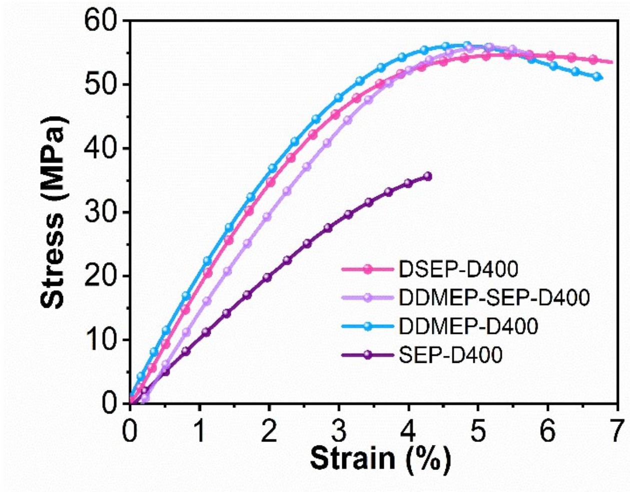


Fig. S25 Representative tensile stress-strain curves of DSEP-D400, DDMEP-SEP-D400, DDMEP-D400 and SEP-D400.

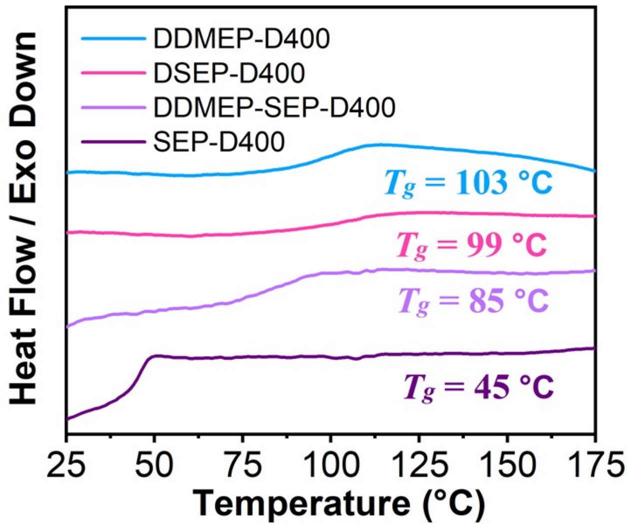


Fig. S26 DSC curves of DSEP-D400, DDMEP-SEP-D400, DDMEP-D400 and SEP-D400.

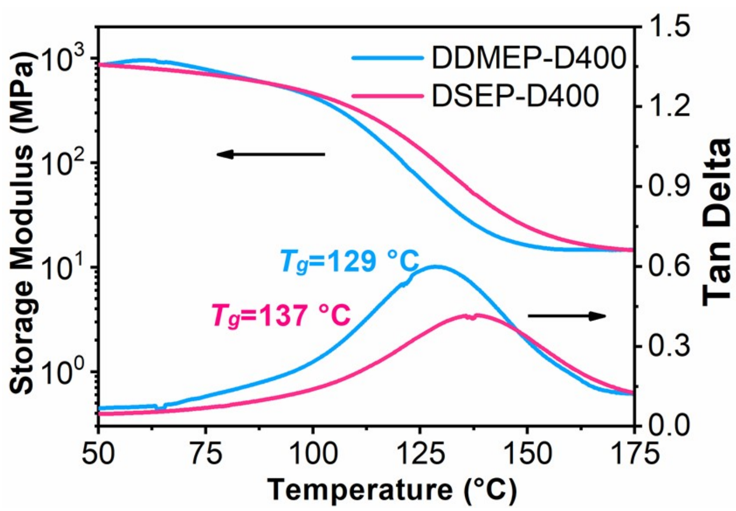


Fig. S27 DMA curves of DDMEP-D400 and DSEP-D400.

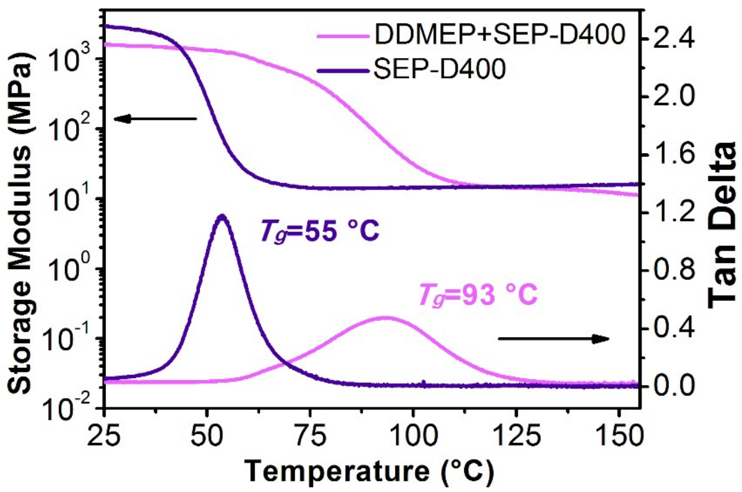


Fig. S28 DMA curves of DDMEP-SEP-D400 and SEP-D400.

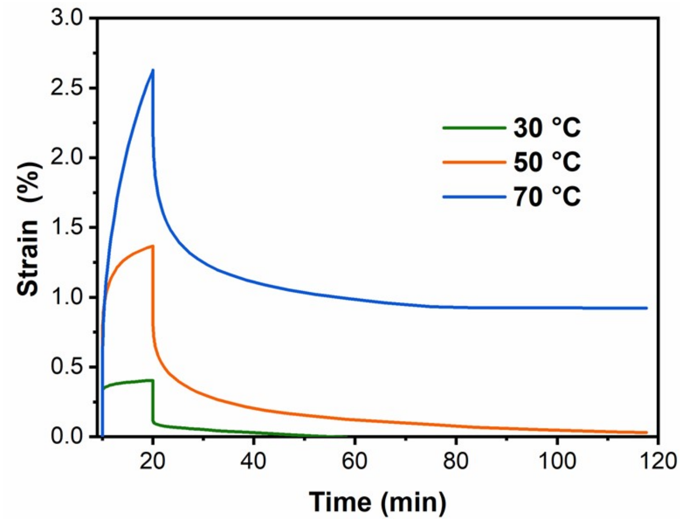


Fig. S29 Creep curves of DSEP -D400.

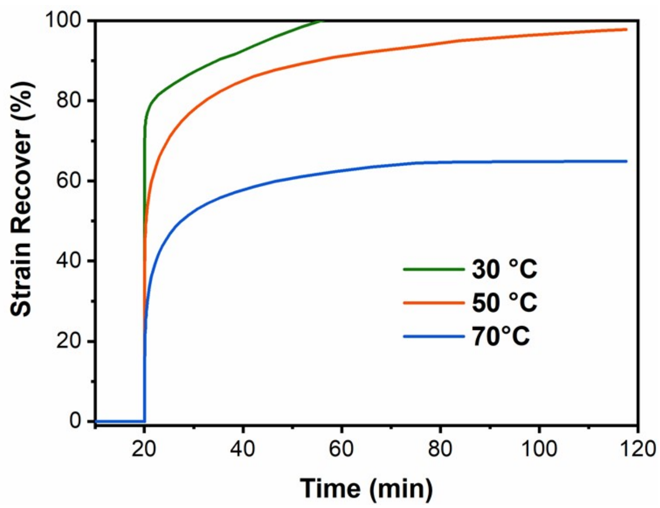


Fig. S30 Strain recovery of DSEP -D400.

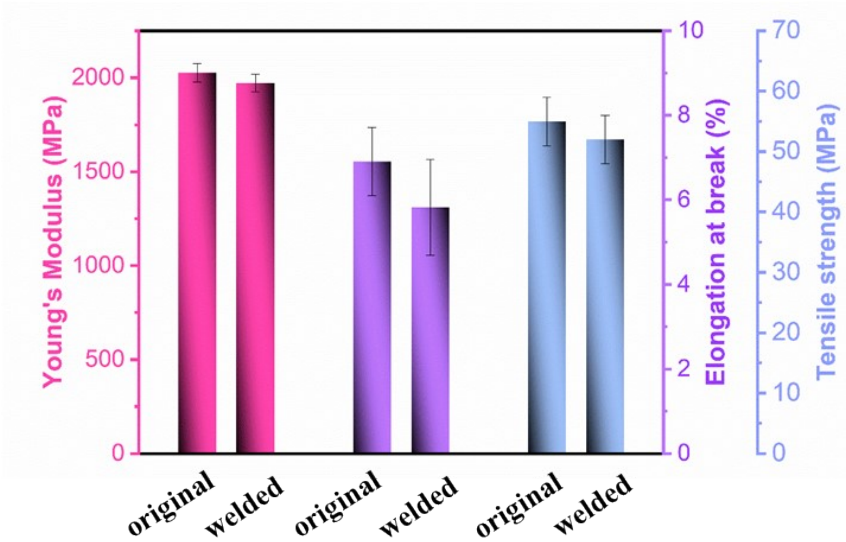


Fig. S31 Young's modulus, elongation at break and tensile strength of the original and welded DSEP-D400.

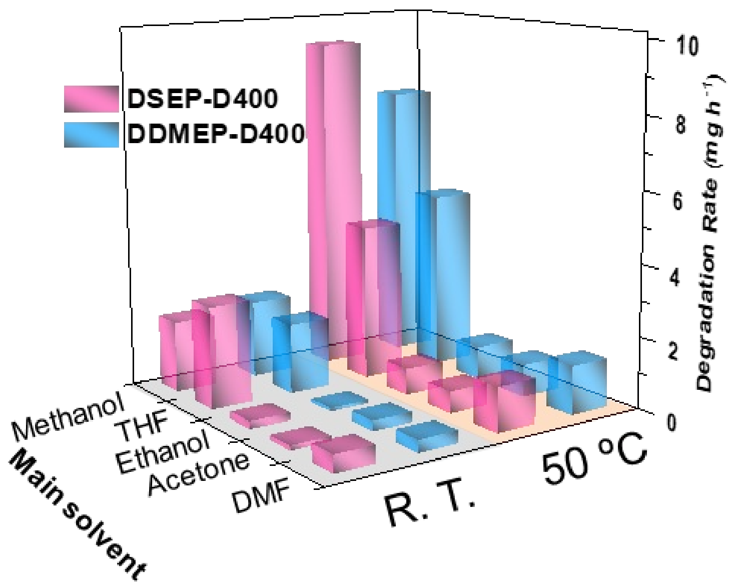


Fig. S32 Degradation rate of DDMEP-D400 and DSEP-D400 in 1 M HCl water/main solvent (2/8, v/v) solution with different main solvent at room temperature and 50 °C.

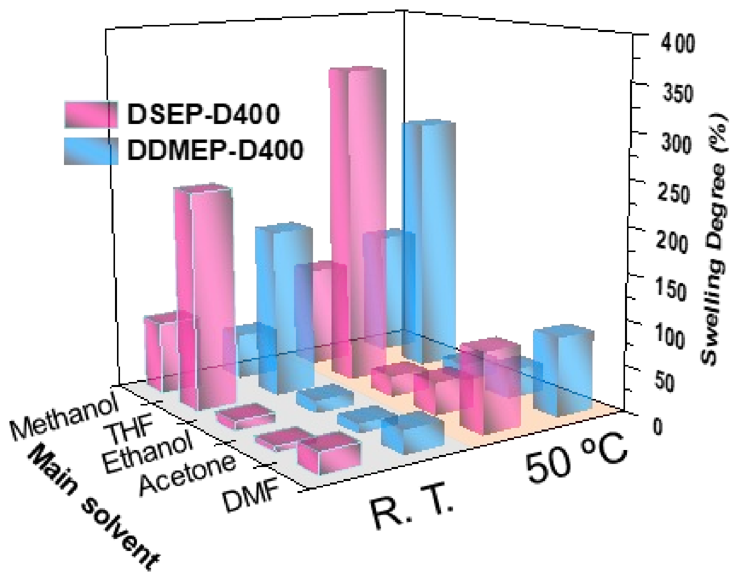


Fig. S33 Swelling degree of DDMEP-D400 and DSEP-D400 in water/main solvent (2/8, v/v) solution with different main solvent at room temperature and 50 °C.

Table S1 Formulations of different samples.

Sample	DSEP (g)	DDMEP (g)	SEP (g)	D400 (g)
DSEP-D400	5.69	/	/	2.00
DDMEP-D400	/	5.19	/	2.00
DDMEP-SEP-D400	/	2.59	1.81	2.00
SEP-D400	/	/	3.62	2.00

Table S2 Peak temperatures of the non-isothermal DSC curves of different curing systems at different heating rates and their activation energies (E_as).

Sample	T_p under different heating rates (K)				E_as (kJ mol^{-1})	
	5 °C min^{-1}	10 °C min^{-1}	15 °C min^{-1}	15 °C min^{-1}	Kissinger	Ozawa
DSEP	409	423	433	439	64.9	67.9
DDMEP	403	418	426	433	61.5	65.2
SEP	393	402	412	419	67.4	70.8

Table S3 Mechanical Properties of DSEP-D400 before and after recycling.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Original	2072±49	55±7	6.91±0.81
Hot press-5 min	1920±62	47±4	2.95±0.36
Hot press-10 min	1980±48	53±4	5.93±0.49
Hot press-20 min	2040±35	56±5	6.15±0.61
Welding	1973±46	52±4	5.82±0.37

Table S4 Mechanical properties of different samples.

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
DSEP-D400	2072±49	55±7	6.91±0.81
DDMEP-D400	2170±73	56±4	6.77±0.72
DDMEP-SEP-D400	1869±67	56±4	5.75±0.48
SEP-D400	1140±86	36±6	4.28±0.55
DER331-D400[1]	1186±14	36±3	6.1±0.3

Table S5 Thermal properties of different samples.

Sample	T_g (°C, DSC)	T_g (°C, DMA)	E' (MPa)	ν_e (mol cm^{-3})	$T_{d5\%}$ (°C)	$T_{d30\%}$ (°C)	R_{800} (%)	T_s (°C)
DSEP-D400	99	137	14.33	1274	273	322	27.08	148
DDMEP-D400	103	129	14.74	1315	279	354	32.69	159
DDMEP-SEP-D400	85	93	14.47	1465	303	350	25.21	162
SEP-D400	45	55	13.72	1536	290	327	11.92	153
DER331-D400[1]	53	55	8.77	1068	367	388	6.39	186

$$T_s = 0.49\left[T_{d5\%} + 0.6\left(T_{d30\%} - T_{d5\%}\right)\right]$$

References

1 X. Xu, S. Ma, S. Wang, J. Wu, Q. Li, N. Lu, Y. Liu, J. Yang, J. Feng and J. Zhu, *J. Mater. Chem. A*, 2020, **8**, 11261-11274.