Tailoring the Biobased Polythiourethane Crosslinking Networks with Flame-Retardancy and Remote Ultrafast Infrared "Welding" Performance

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Characterizations

Fourier transform infrared (FT-IR). FT-IR spectra were obtained on a Nicolet 6700 infrared spectrometer used to analyze the chemical structure of eugenol, PPDC, BEP, DODT, BEP-SH, and the crosslinked PTU in total reflection mode. The scanning range was 4000-500 cm^{-1} and the number of scanning was 128 times.

Nuclear Magnetic Resonance (NMR). ^{1}H NMR and ^{31}P NMR spectra of BEP-SH were recorded on a 400 MHz AVANCE III HD spectrometer (Bruker, Switzerland) using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal standard.

X-ray diffraction (XRD). To investigate the inherent interactions of Ti_3AlC_2 and F-MXene, X-ray diffraction patterns were recorded by AXS D8 diffractometer (Bruker, German) using Cu-Kα radiation (λ = 1.5406 Å, 40 Kv, 20 mA) and 0.2 theta scan ranging from 5° to 65°.

Scanning electron microscopy (SEM). The microstructures of Ti_3AlC_2, M-MXene, F-MXene, and MXene-SH were investigated by SEM (S-4800, HITACHI, Japan). All samples were sputtered with a layer of gold before observation.

Thermogravimetric analysis (TGA). TGA was carried out on an 1100SF TA Instruments apparatus (Mettler-Toledo, Switzerland) under nitrogen at a 50 mL/min flow rate and a 20 °C/min heating ramp from 40 °C to 800 °C. The mass for each sample was around 5-10 mg.

Dynamic mechanical analysis (DMA). The evaluation of T_g temperatures, storage modulus, loss modulus, and tan δ for the crosslinked PTU was carried out on a TA

Instrument (TA Q800, USA) at a heating rate of 3 °C/min from -20 °C to 140 °C. Samples with dimensions of 30 mm×10 mm×2 mm were tested by using a film tensile clamp, frequency of 1 Hz, and amplitude of 10 μm.

Differential scanning calorimetry (DSC). The glass transition temperature (T_g) of the crosslinked PTU (about 5-10 mg) was studied by DSC measurements (DSC-8000, PE Instrument, USA). The composites were heated from -40 °C to 120 °C at a 20 °C/min heating rate under a nitrogen flow.

Tensile test. The tensile test of standard dumbbell crosslinked PTU was performed by using a universal material testing machine (Instron 5967, USA), according to ASTM D638, at a crosshead rate of 50 mm/min. All samples were tested for at least 5 repetitions, and their average value for the mechanical parameters was calculated.

Limiting oxygen index (LOI). The LOI tests were carried out with a JF-3 oxygen index tester (Jiangning Analysis Instrument Company, China) according to ASTM D2863-97 standard, with sheet dimensions 100×10×3 mm^3. The LOI measurement for each specimen was repeated five times.

The vertical burning test (UL-94). UL-94 vertical burning tests were carried out on a CZF-4 type vertical burning tester (Shangyuan Analysis Instrument Company, China) according to ASTM D3801-2010, with sheet dimensions of 130×13×3 mm^3. The measurement for each specimen was repeated five times.

Thermogravimetry-infrared (TG-IR). The TG-FTIR (PE TGA4000, USA) was used to test the pyrolysis volatiles of B10T0-THDI, B10T0-TTI, and B8T2-TTI under N_2 atmosphere. The samples were heated from the 30 to 800 °C.

Optical microscope. The scratch changes on the surface of the sample were observed by an optical microscope, and a scratch of a certain width was scratched on the surface of the sample. The self-healing of surface scratches of crosslinked PTU B8T2-TTI and PTU/MXene composites under remote infrared light irradiation (light intensity was 2 W/cm^2) was observed.

Table S1 The formula of PTU network and PTU/MXene composites

Samples	BEP-SH (g)	TEMPIC (g)	THDI (g)	TTI (g)	MXene-SH (g)
B10T0-THDI	10	/	4.13 g	/	/
B10T0-TTI	10	/	/	3.006	/
B9T1-TTI	10	1.1	/	3.775	/
B8T2-TTI	10	2.5	/	4.754	/
B8T2-TTI-0.25M	10	2.5	/	4.758	0.043
B8T2-TTI-0.5M	10	2.5	/	4.762	0.086

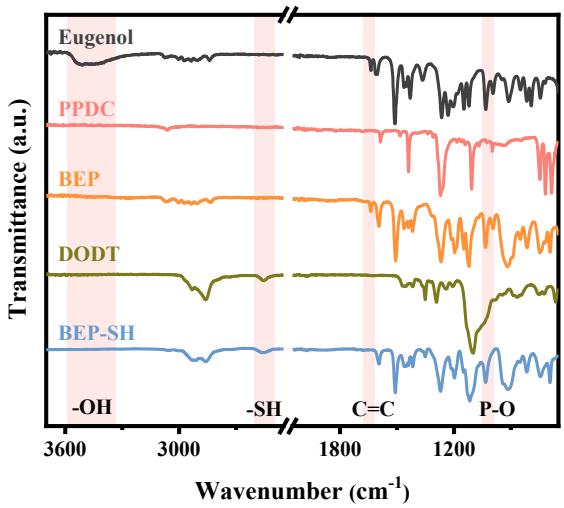

Figure S1 FT-IR of monomer BEP-SH

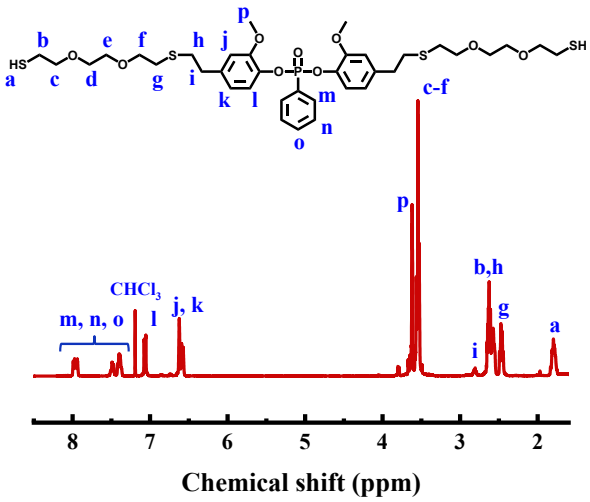

Figure S2 ^{1}H NMR of monomer BEP-SH

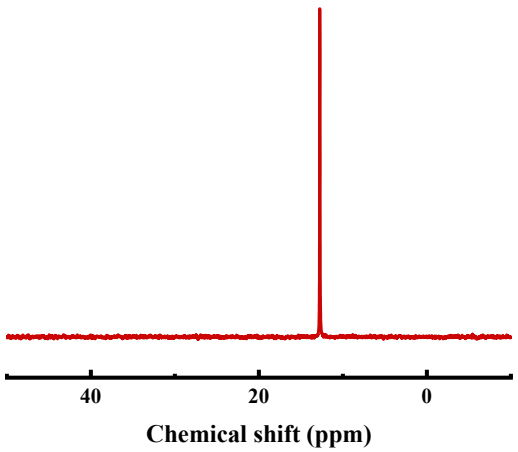

Figure S3 ^{31}P NMR of monomer BEP-SH

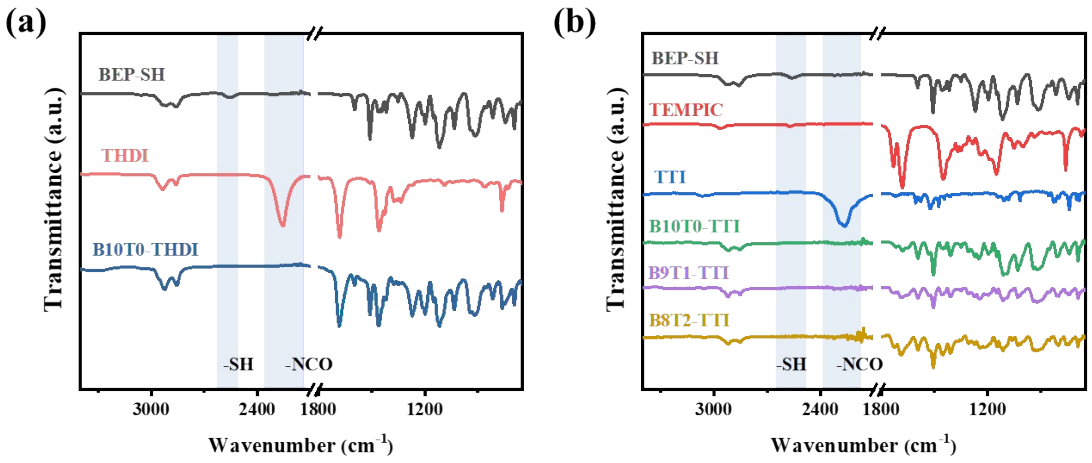

Figure S4 The FTIR spectra of polythiourethanes before and after curing (a) B10T0-THDI, (b) B10T0-TTI, B9T1-TTI, and B8T2-TTI

Table S2 Mechanical properties of the cross-linked PTU

Sample	Tensile Strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
B10T0-THDI	23.7±1.4	225.3±3.8	17.4±1.0
B10T0-TTI	52.7±2.8	8.7±1.6	1638.9±47.3
B9T1-TTI	60.8±3.6	7.3±1.3	1826.2±59.6
B8T2-TTI	65.0±2.1	6.2±0.9	1951.4±27.8

Table S3 Thermal properties of the cross-linked PTU

Samples	$T_{5\%}$ (℃)	$R_{800\,℃}$ (%)	T_{dmax} (℃)	T_g (℃) DSC	T_g (℃) DMA	E' at 25 ℃ (MPa)	v_e (mol/m^3)
B10T0-THDI	312.0	5.4	354.3/471	16.7	32.8	773	825
B10T0-TTI	310.0	16.5	349.7	49.7	75.1	1317	485
B9T1-TTI	294.7	18.3	350.3	55.8	81.5	1350	807
B8T2-TTI	279.3	19.8	353.7	61.7	83.4	1368	971

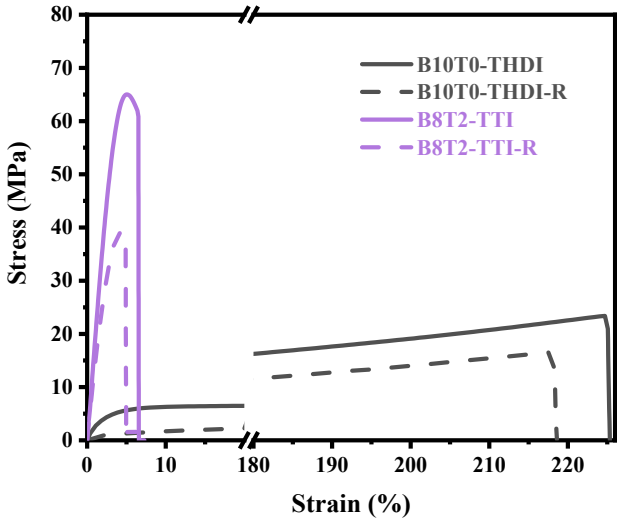

Figure S5 Tensile stress-strain curves of original and reprocessed B10T0-THDI and B8T2-TTI

The tensile strength of the samples after repeated processing had decreased. The tensile strength of B10T0-THDI and B8T2-TTI after secondary processing maintained 70.7 % and 60.1 % of the tensile strength of the original sample. The thiocarbamate bond can be exchanged during the reprocessing process, while other covalent bonds on the main chain cannot be repaired after being destroyed, resulting in a decrease in the crosslinking density, which made the tensile strength significantly reduced. The tensile strength recovery rate of B8T2-TTI was lower than that of B10T0-THDI.This was mainly because the rigid benzene ring structure in TTI limits the movement of polymer segments, and the thiocarbamate bond was difficult to move to the interface to undergo bond exchange, making the reprocessing efficiency of B8T2-TTI lower than that of B10T0-THDI.

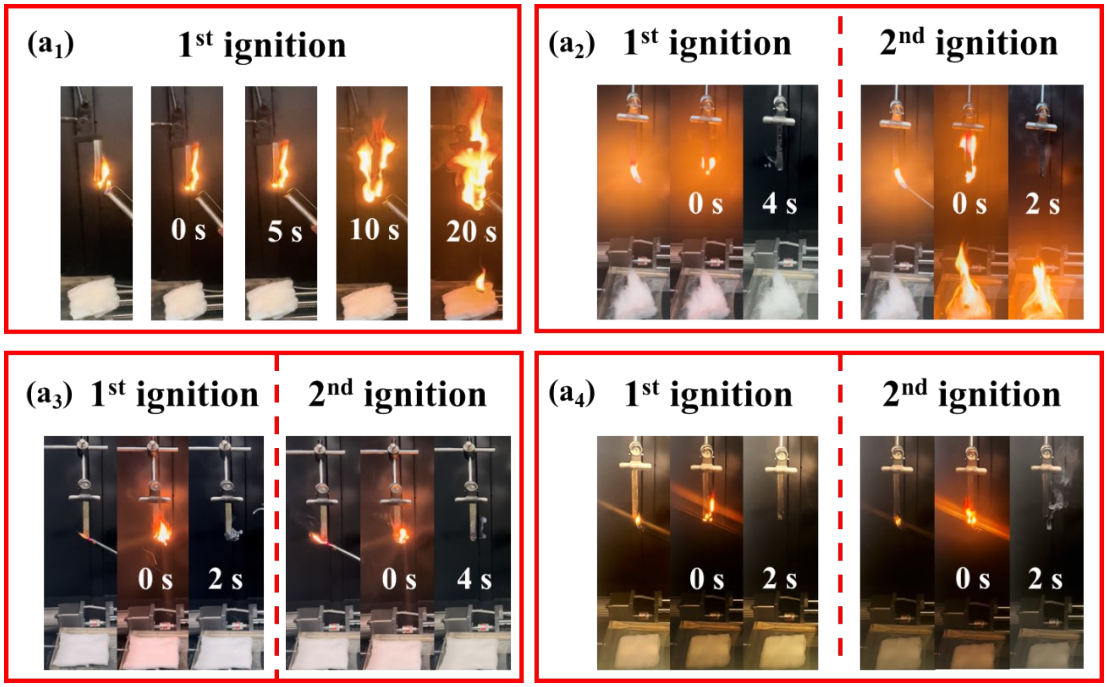

Figure S6 Digital photographs of vertical combustion of the crosslinked PTU (a_1) B10T0-THDI, (a_2) B10T0-TTI, (a_3) B9T1-TTI, (a_4) B8T2-TTI

Table S4 The LOI value and UL-94 rating of the crosslinked PTU

Samples	LOI (%)	UL-94			
		t_1+t_2 (s)	Dripping	Cotton Ignition	Rating
B10T0-THDI	21.2	＞30	Yes	Yes	No Rating
B10T0-TTI	27.3	6	Yes	Yes	V-2
B9T1-TTI	27.8	6	No	No	V-0
B8T2-TTI	28.4	4	No	No	V-0

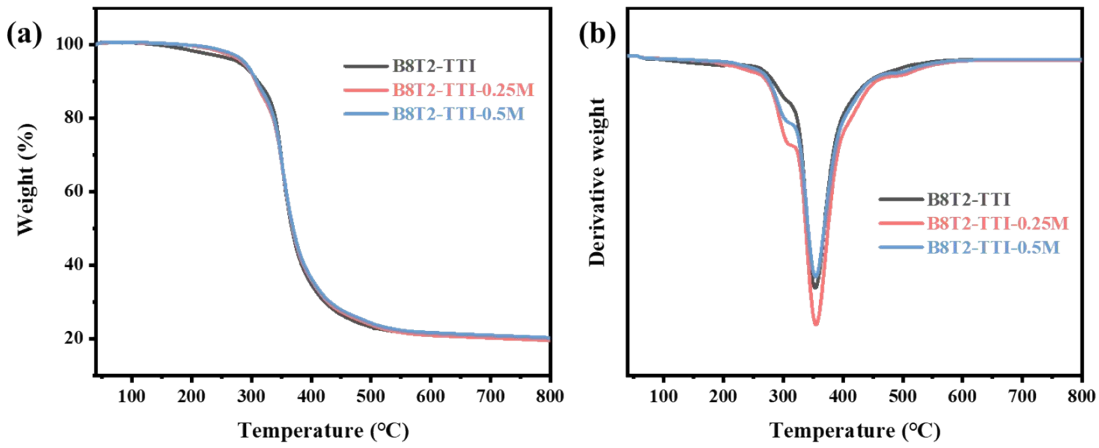

Figure S7 (a) TGA and (b) DTG curves of PTU/MXene composites

Table S5 Thermal and mechanical properties of the PTU/MXene composites

Samples	$T_{5\%}$ (℃)	$R_{800\,℃}$ (%)	T_{dmax} (℃)	Tensile Strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
B8T2-TTI	279.3	19.8	353.7	65.0±2.1	6.2±0.9	1.95±0.03
B8T2-TTI-0.25M	287.3	19.4	355	66.2±2.4	4.5±0.2	2.26±0.06
B8T2-TTI-0.5M	289.3	20.2	354.3	66.4±1.9	3.7±0.1	2.45±0.08

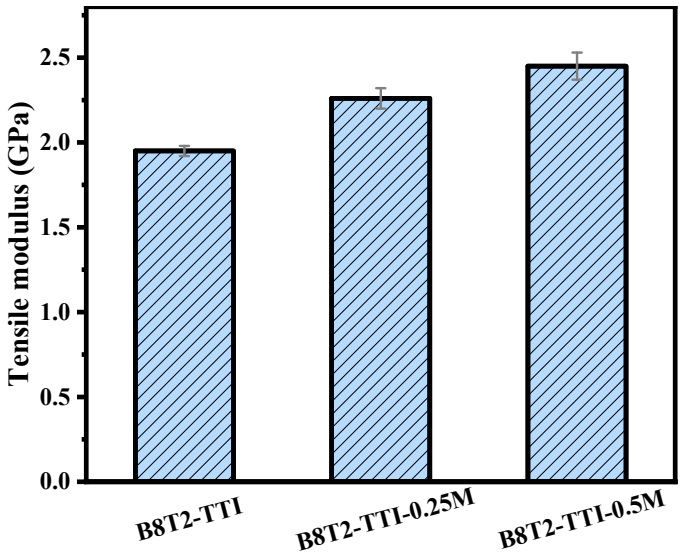

Figure S8 Tensile modulus of the PTU/MXene composites