

Recyclable Tough Thermoset with Imide-Hexahydrotriazine Structure

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Supporting Information

1. Materials

4, 4'-oxydianiline (ODA, 98%), 2, 2-bis[4-(4-aminophenoxy) phenyl]propane (BAPP, 98%), 4, 4'-Oxydiphthalic Anhydride (ODPA, 98%), paraformaldehyde (PFA, 96%), sodium bicarbonate (NaHCO_3 , 99%), meta-xylene (C_8H_{10} , 99%), acetone ($\text{C}_3\text{H}_6\text{O}$, 99+%), N, N-Dimethylacetamide ($\text{C}_4\text{H}_9\text{NO}$, 99.8%), 1-Methyl-2-pyrrolidinone ($\text{C}_5\text{H}_9\text{NO}$, 99%), dimethyl sulfoxide ($(\text{CH}_3)_2\text{SO}$, 99%), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, 99%), dichloromethane (CH_2Cl_2 , 99.9%) were purchased from Aladdin Reagent Co, Ltd. The concentrated hydrochloric acid (HCl , 37%) was supplied by Xi Long Scientific Ltd.

2. Characterization

Fourier transform infrared spectrum (FT-IR) was performed on a Nicolet iS10 FTIR spectrometer (Thermo Scientific, America). Nuclear magnetic resonance (NMR) spectra were recorded in $\text{DMSO}-d_6$ on a Bruker AVF400 instrument (400 MHz). Scanning electron microscope (SEM) was utilized to characterize the morphologies of PHT thermosets before and after degradation (SUPRA 55 SAPPHIRE, Carl Zeiss). Thermogravimetric analysis (TGA) was conducted to determine the thermal stabilities of PHT thermosets with temperature from 20 to 810 °C in argon atmosphere at a heating rate of 10 °C/min (NETZSCH, Germany). Molecular weight distribution of polyimides oligomers was characterized by Gel Permeation Chromatography (GPC, Viscotek TDA). The powder X-ray diffraction (PXRD) pattern was recorded by an X' Pert PRO XRD instrument (PANalytical, Netherlands). Dynamic mechanical analysis (DMA) was performed using a tensile film mode (Q800 TA Instrument, USA) under the N_2 protection with a heating rate of 5 °C/min. The testing specimens was cut into a

dimension of $20 \times 3 \times 0.1 \text{ mm}^3$. Differential scanning calorimetry (DSC) analysis was implemented on a STA449F3 instrument (NETZSCH, Germany) under N_2 atmosphere with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$. The mechanical properties of PHT thermosets were evaluated on a universal tensile test machine (INSTRON5569, USA) at a cross-head speed of $2 \text{ mm}/\text{min}$ at room temperature. The tensile strength and young's modulus were recorded on account of an average of at least five specimens for accuracy. The UV photoaging test was performed in an UV-accelerated aging box, where the intensity of the UV light, the experimental temperature, and the irradiation distance were set as $960 \text{ W}/\text{m}^2$, $50 \text{ }^\circ\text{C}$, and 50 cm , respectively. The wavenumber of UV light was in the range of $300\text{--}500 \text{ nm}$. The samples were successively taken out from the UV aging box with the irradiation time interval setting at 48 h . Finally, the anti-UV properties of various resin samples were evaluated by the universal tensile test machine (INSTRON5569, USA) at a cross-head speed of $2 \text{ mm}/\text{min}$ at room temperature after different UV-accelerated aging times.

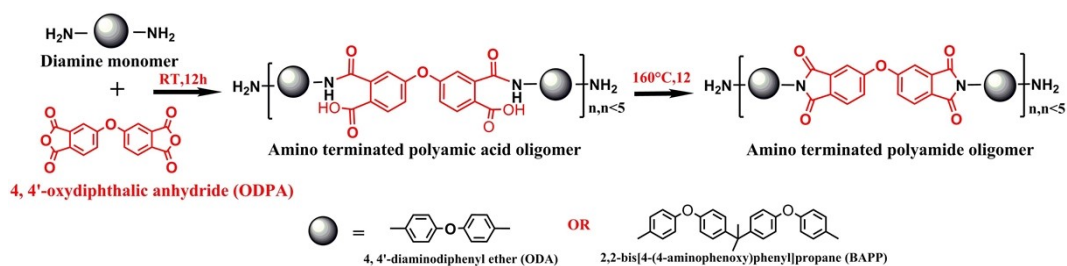


Fig. S1. The two-step preparation process of amino-capped polyimide oligomers.

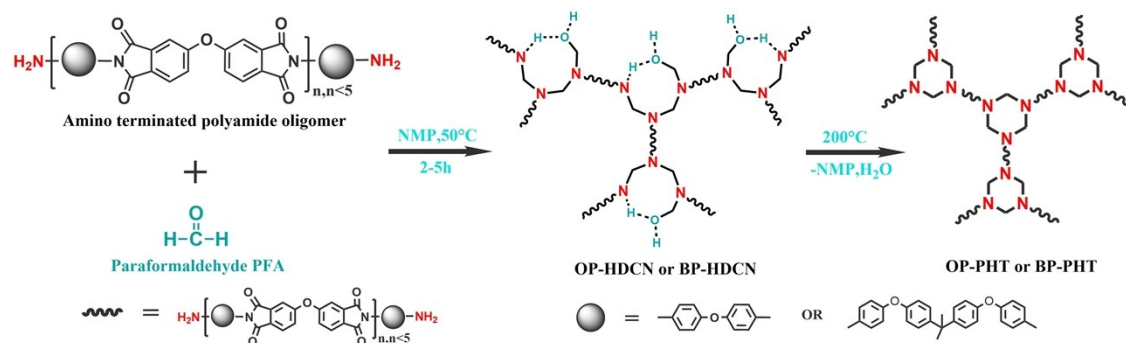


Fig. S2. The two-stage fabrication route of PHT thermosets based on the reaction between amino-capped polyimide oligomers and PFA.

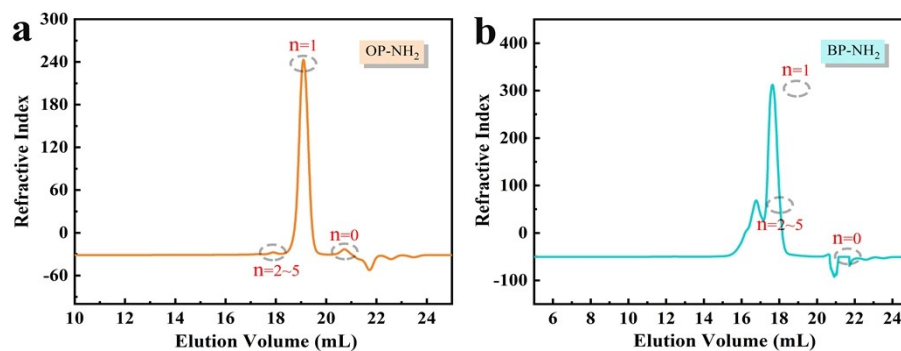


Fig. S3. GPC curves of **a** OP-NH₂ And **b** BP-NH₂. GPC data of the specimens were tested and collected in THF solvent with the elution rate keeping at 1.0 mL/min.

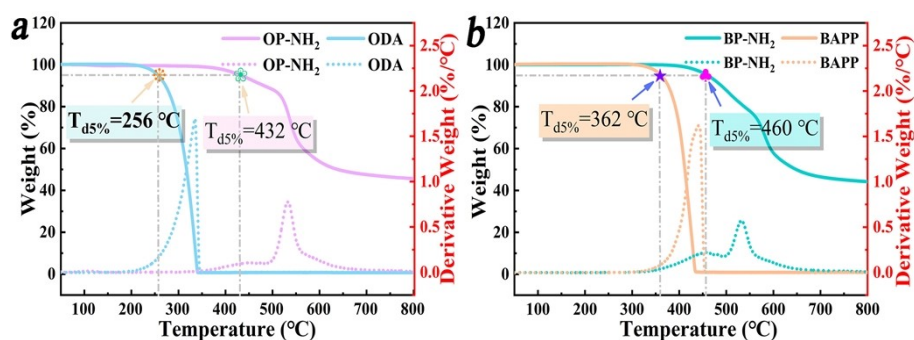


Fig. S4. TGA curves of **a** ODA and OP-NH₂ under N₂ atmosphere, TGA curves of **b** BAPP and BP-NH₂ under N₂ atmosphere.

Table S1. Qualitative solubility study of diamine monomer, original and recycled oligomer products

Sample	DMAc	DMF	NMP	DMSO	THF	CH ₂ Cl ₂	Acetone	Ethanol	H ₂ O
ODA	++	++	++	++	++	++	++	++	++
BAPP	++	++	++	++	++	++	++	++	++
OP-NH ₂	++	++	++	++	+	+	+	+	-
BP-NH ₂	++	++	++	++	++	++	+	+	-
ROP-NH ₂	++	++	++	++	+	+	+	+	-
RBP-NH ₂	++	++	++	++	++	++	+	+	-

ROP-NH₂: recycled oligomer from OP-PHT. RBP-NH₂: recycled oligomer from BP-PHT. All solubility tests are measured at an initial concentration of 100 mg/mL in various solvents at 25 °C. (++): soluble at room temperature; (+): partially soluble at room temperature (40–60 mg/mL); (-): partially soluble on heating (20–40 mg/mL). DMAc: dimethylacetamide; DMF: N, N-dimethylformamide; NMP: N-methyl pyrrolidone; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

According to the integral areas of peaks H1 and H6 in ¹H NMR spectrum shown in **Fig. 2a**, the number average molecular weight (M_n) and the degree of polymerization (n) of OP-NH₂ were calculated via the following formula.

$$n = \frac{\text{Number of repeating units}}{\text{Number of molecular chains}} = \frac{\text{Area}(H1)/2}{\text{Area}(H6)/4}$$

(S-1)

$$M_n = M_{\text{repeating units}} \times n + M_{\text{ODA}} = 474 \times n + 200 \quad (\text{S-2})$$

Because there were 2H in ODA of in each repeating unit, so the number of repeating units was obtained by normalizing peak (H1) by a factor of 2. Similarly, the number of chains is calculated by normalizing Area (H6) with a factor of 4 owing to each chain has 4H in the amine end groups.

Besides, according to the integral areas of peaks H1 and H7 in ¹H NMR spectrum shown in **Fig. 2b**, the number average molecular weight (M_n) and the degree of polymerization (n) of BP-NH₂ were calculated via the formula S-1 and S-2. The number of chains is calculated by normalizing Area (H7) with a factor of 4 owing to each chain has 4H in the amine end groups. Therefore, the Area (H6) should be replaced by Area (H6) and M_{ODA} should be replaced by M_{BAPP} when calculating the M_n and n of BP-NH₂.

Table S2. The theoretical, actual molecular weights and PDI values of OP-NH₂ and BP-NH₂ obtained from chemical structure, ¹H NMR and GPC tests

Polyimide	Theory	¹ H NMR		GPC	
	M_n (g/mol)	M_n (g/mol)	M_n (g/mol)	M_w (g/mol)	PDI
OP-NH ₂	674	810.08	741.49	757.78	1.02
BP-NH ₂	1094	1385.00	1790.17	1857.74	2.71

Table S3. Performance parameters of the PHT thermosets and composites and a comparison with other analogous resins and composites: Thermal stability, mechanical property and

recyclability

Samples	T _g (°C)	T _{d5%} (°C)	Tensile Strength (MPa)	Elongation at break (%)
^a DGEBA/DDM	~155	~382	~75	~4.4
^b TGDDM/DDS	~220	~306	~58	~1.6
The acetal epoxy ^{1,2}	21–110	225–273	52.5–65.4	3.7–8.5
The disulfide epoxy ^{3,4}	~130	~300	~88	~7.1
The polyimine ^{5,6}	18–135	--	10–64	5–150
^c PETI-5 ^{7,8}	270	499	129.6	32
ODA-PHT ⁹	193	238	~90	~3
BAPP-PHT ¹⁰	200	368	124	3.8
OP-PHT (this work)	211	433	116	3.8±0.19
BP-PHT (this work)	207	468	129	11.6±0.58

Composites	ILSS (MPa)	Flexural stress (MPa)	Recycled CFs' surface chemical structure	Recovery of matrix main raw materials
^a DGEBA/DDM	--	--	damaged	No
^b TGDDM/DDS	--	--	damaged	No
The acetal epoxy/62vol% cross-ply CF ^{1,2}	66-73	1302	Unchanged	No
The disulfide epoxy/ plain weave CF ^{3,4}	37.3	595.4	Not reported	NO
The polyimine/ 60–75 wt% twill weave CF ^{5,6}	32.4–38.1	142–255	Not reported	Yes
ODA-PHT ⁹	--	--	--	No
BAPP-PHT ¹⁰ (The cross-ply CF/PHT composites)	54.8	827.9	Unchanged	Yes
OP-PHT (this work)	--	--	Unchanged	Yes
BP-PHT (this work, The cross-ply CF/PHT composites)	53	649	Unchanged	Yes

^a: DGEBA/DDM stands for the tetradiglycidyl diaminodiphenylmethane/diaminodiphenylsulfone epoxy resin system.

^b: TGDDM/DDS stands for the tetradiglycidyl diaminodiphenylmethane/diaminodiophenylsulfone epoxy resin system.

^c: PETI-5 stands for a polyimide whose imide oligomers are synthesized from the reaction of 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,4-diaminodiphenyl ether (ODA) and 1,3-bis(3-aminophenoxy)benzene (APB). And the imide oligomers are terminated by 4-Phenylethynylphthalic anhydride (PEPA). When phenylethynyl groups are placed on the ends of the oligomers (PETI), the polyimide is called PETI-5.

Table S4. Chemical stabilities and corresponding weight changes of OP-PHT in different organic solvents , acidic, alkali and salt solutions under specific conditions

Number	Conditions	pH values	Weight changes (%)
1	DMAc (96 h, 25 °C)	7	+ 3.11
2	NMP (96 h, 25 °C)	7	+ 3.34
3	Acetone (96 h, 25 °C)	7	+ 0.52
4	THF (96 h, 25 °C)	7	+ 0.61
5	H ₂ O (96 h, 25 °C)	7	+ 0.13
6	HCl solution (96 h, 25 °C)	3	Not decomposed
7	HCl solution (96 h, 25 °C)	2	Not decomposed
8	H ₂ SO ₄ solution (96 h, 25 °C)	3	Not decomposed
9	H ₂ SO ₄ solution (96 h, 25 °C)	2	Not decomposed
10	NaOH solution (96h, 25 °C)	12	Not decomposed
11	NaOH solution (96h, 25 °C)	13	Not decomposed
12	NaCl solution (96h, 25 °C)	7	Not decomposed

Table S5. Chemical stabilities and corresponding weight changes of BP-PHT in different organic solvents, acidic, alkali and salt solutions under specific conditions

Number	Conditions	pH values	Weight changes (%)
1	DMAc (96 h, 25°C)	7	-0.62
2	THF (96 h, 25°C)	7	-0.41
3	Acetone (96 h, 25°C)	7	+3.24
4	Dichloromethane (96 h, 25°C)	7	+ 2.03
5	H ₂ O (96 h, 25°C)	7	+ 0.21
6	HCl solution (96 h, 25°C)	3	Not decomposed
7	HCl solution (96 h, 25°C)	2	Not decomposed
8	H ₂ SO ₄ solution (96 h, 25°C)	3	Not decomposed
9	H ₂ SO ₄ solution (96 h, 25°C)	2	Not decomposed
10	NaOH solution (96h, 25 °C)	12	Not decomposed
11	NaOH solution (96h, 25 °C)	13	Not decomposed
12	NaCl solution (96h, 25 °C)	7	Not decomposed

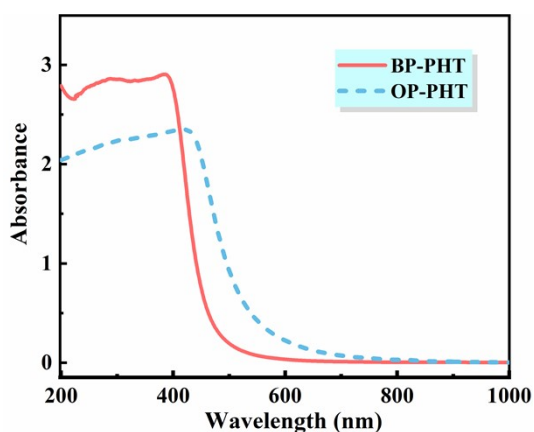


Fig. S5. The absorbance spectra of OP-PHT and BP-PHT.

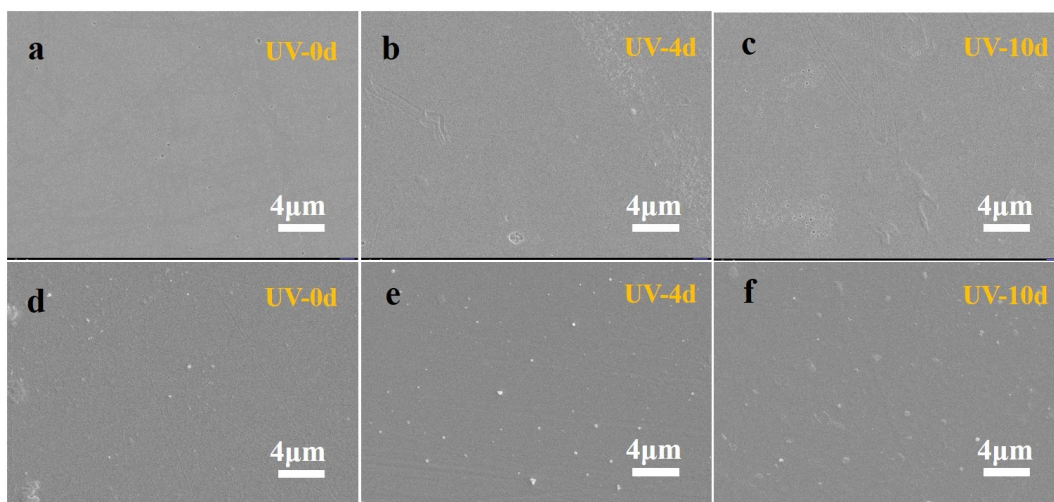


Fig. S6. SEM images of the surface morphology for OP-PHT (a, b, c) and BP-PHT (d, e, f) treated by UV light over different time.

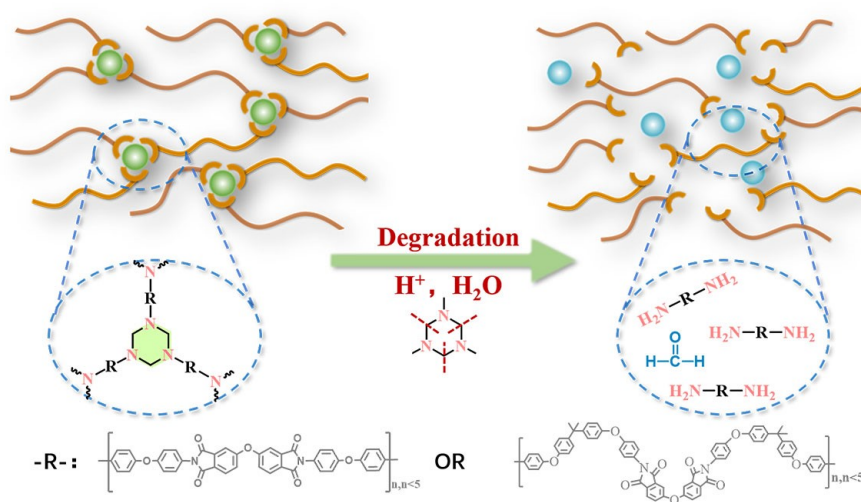


Fig. S7. The scheme of degradation processes of BP-PHT thermosets

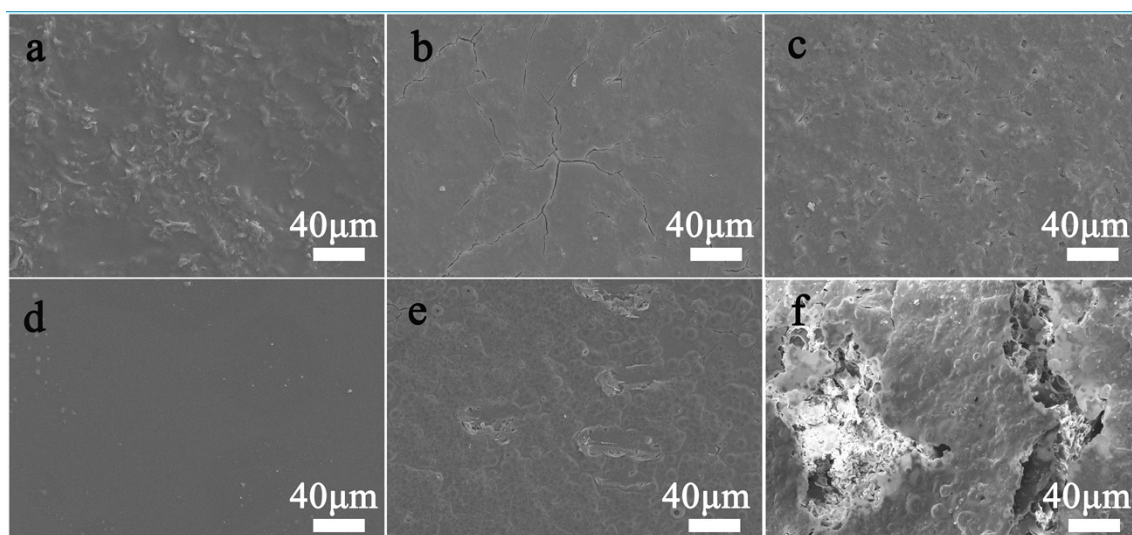


Fig. S8. SEM images of the surface morphology for OP-PHT separately immersed in 1 M HCl/acetone for different times at 25 °C. **a** 0 h, **b** 2 h and **c** 4 h. SEM images of the surface morphology for BP-PHT separately immersed in and 1 M HCl/THF at 25 °C, **d** 0 min, **e** 40 min and **f** 80 min, respectively.

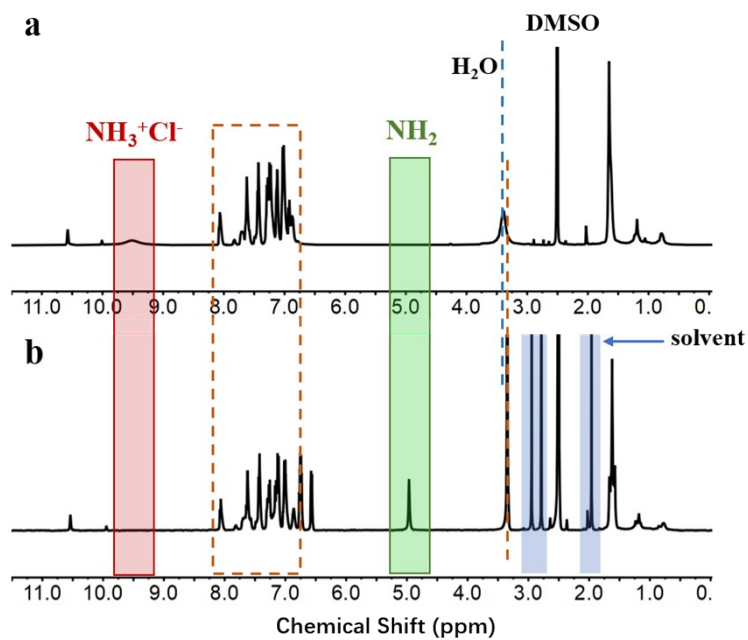


Fig. S9. ^1H NMR spectra of $\text{RBP-NH}_3^+\text{Cl}^-$ and RBP-NH_2

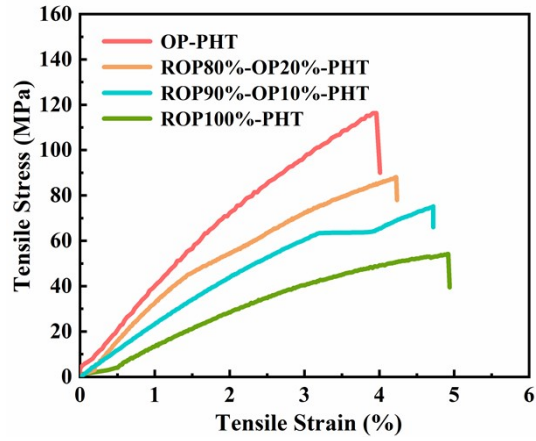


Fig. S10. The tensile stress-strain curves of OP-PHT and repaired PHT thermosets using recycled starting materials.

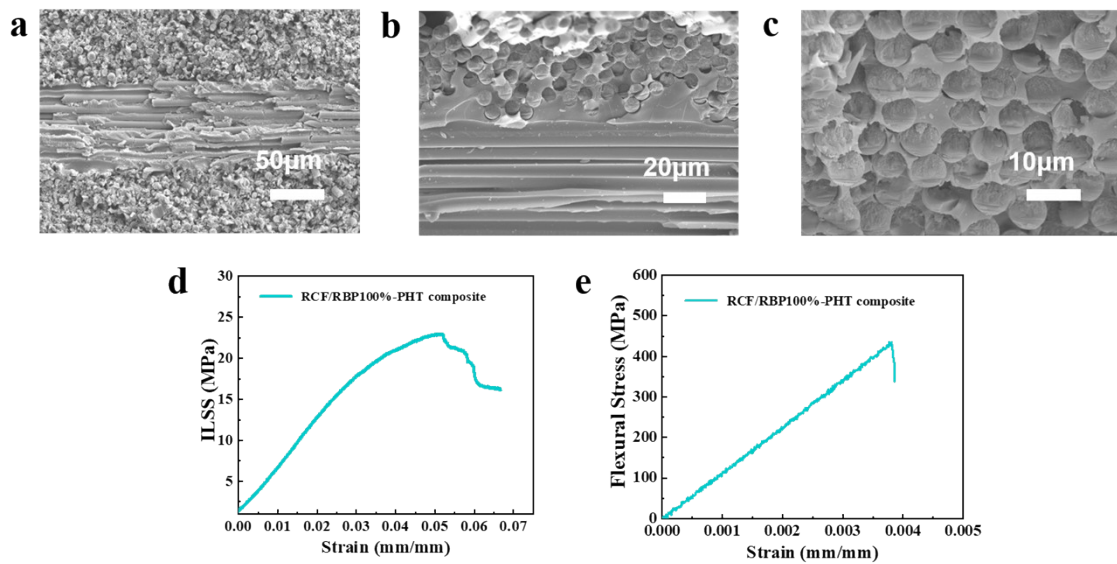


Fig. S11. a-c SEM images of fracture and surface topographies of composite laminates. d-e Representative ILSS and flexural stress-strain curves of RCF/RBP100%-PHT composite laminates.

Table S6. Atomic concentration on the surface of the virgin CF and recycled CF.

Sample	Atomic conc. (%)		
	C	N	O
Virgin CF	84.97	2.96	12.06
Recycled CF	84.49	2.16	13.35

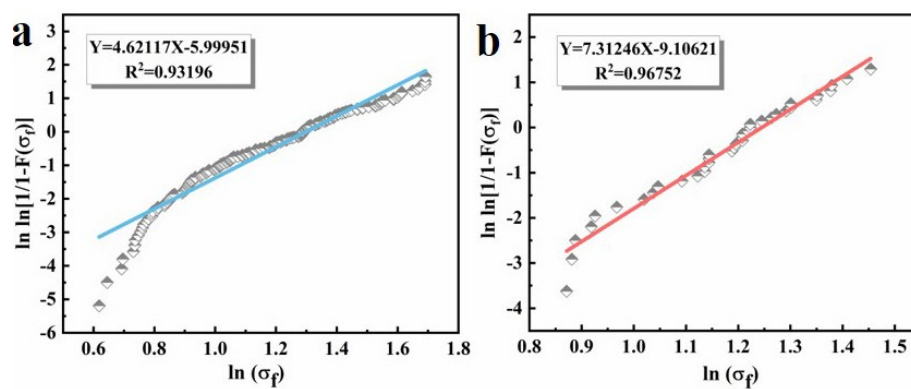


Fig. S12. The Weibull distribution plot of tensile strength of **a** virgin and **b** recycled CF monofilaments.

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