Supporting Information

Malleable and recyclable imide-imine hybrid thermosets: influence of imide structure on material property

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1. Materials and methods

All chemical reagents and solvents were provided by commercial suppliers and used as received unless otherwise stated. 2,5-Dimethyl-1,4-phenylenediamine (DPD), 2,6-Diaminotoluene (DAT), 4,4'-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4'-Oxydiphthalic anhydride (ODPA), 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), Terephthalaldehyde (TPA) were purchased from Energy Chemical Co. Ltd. Triethylenetetramine (TREN) and diethylenetriamine (DETA) are used after low temperature storage. 1-Methyl-2-pyrrolidinone (NMP) and N,N-Dimethylformamide (DMF) were freshly distilled under reduced pressure over phosphorus pentoxide and stored over 4 Å molecular sieves prior to use.

The FT-IR spectra were measured utilizing a Nicolet IS50 FT-IR Spectrometer (Thermo Fisher Scientific). NMR spectra were taken on an AVANCE III 600 NMR spectrometer in deuterated solvents (DMSO-d6). DMSO (2.50 ppm) was used as internal references in ^{1}H NMR. ^{1}H NMR data were reported in order: chemical shift, multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), and number of protons. Solid-state cross polarization magic angle spinning (CP/MAS) NMR spectra were recorded on an Inova 400 NMR spectrometer. Mass spectra were recorded on a UPLC-MS/MS system (Thermo Fisher Scientific, Waltham, United States).

The internal loss factor tan δ was determined on a DMA 242E instrument (NETZSCH, USA). All samples were subjected to the temperature scan mode at a programmed heating rate of 2 °C/min at a single frequency of 1 Hz from room temperature to 200 °C in a tensile mode with strain of 0.1% and preload force of 0.20 N. The glass transition temperature (T_g) was taken from the maximum of the peak in the α-transition region of the tan δ curve.

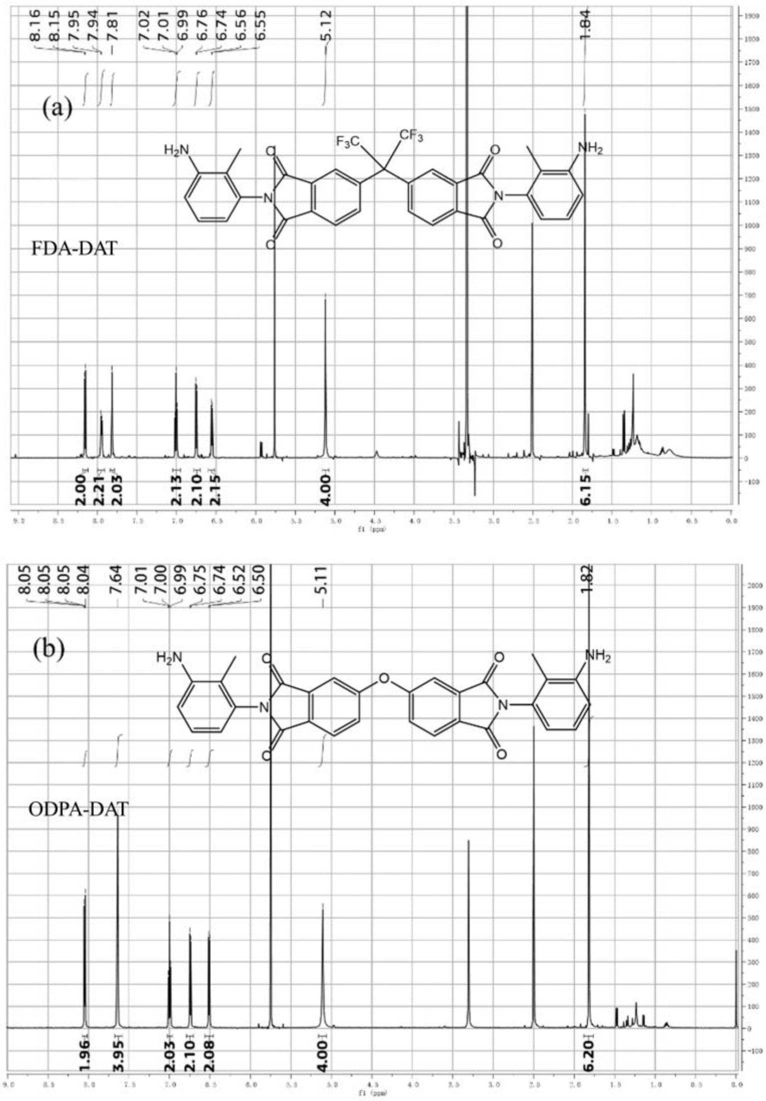
TGA measurements were carried out on a Mettler TGA/DSC/1600LF series thermogravimetric analyzer at a heating rate of 10 °C/min under inert atmosphere from room temperature to 800 °C.

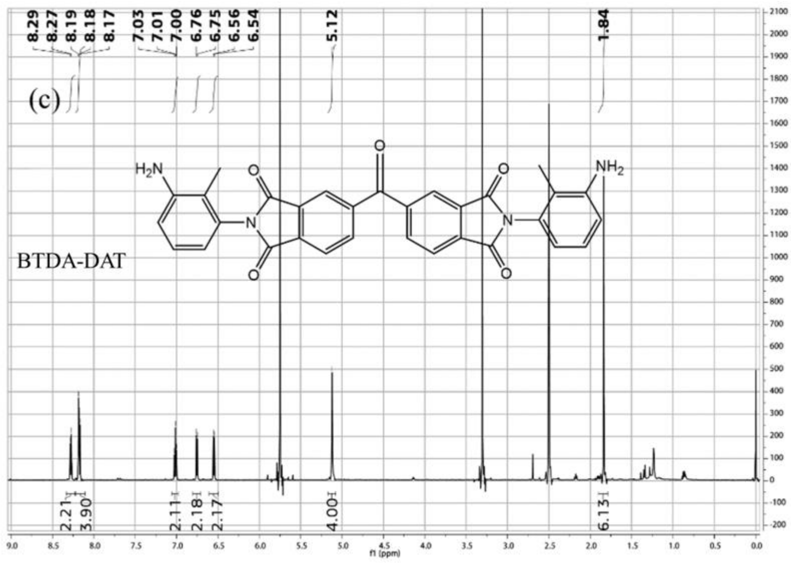
The mechanical properties of imide-imine hybrid films were measured using a

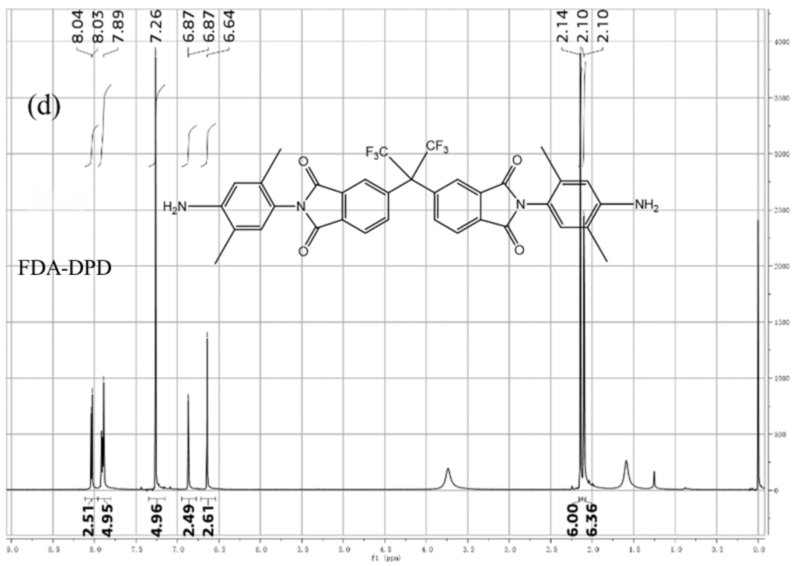
Universal mechanical testing system (model: UTM4304, Shenzhen suns technology stock co. Ltd) on 3 spindle film strips (W=3.225 mm) with a gauge length measured after installing the sample at room temperature. Uniaxial tension load with loading speed of 2 mm/min was used for static tension test. Uniaxial tensile strength test standard was ASTM D638. The tensile modulus was taken as the initial slope of the stress–strain curves.

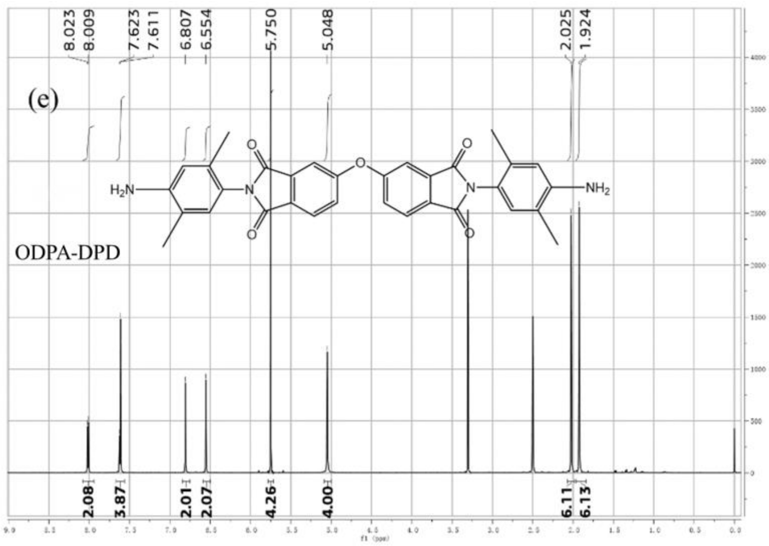
2. Characterization

2.1 NMR spectra of Ims




(c)
BTDA-DAT
8.29 8.27 8.19 8.18 8.17 7.03 7.01 7.00 6.76 6.75 6.56 6.54
5.12
1.84
2.21 3.90 2.11 2.18 2.17 4.00 6.13
f1 (ppm)


(d)
FDA-DPD
8.04 8.03 7.89 7.26 6.87 6.87 6.64
2.14 2.10 2.10
2.51 4.95 4.96 2.49 2.61 6.00 6.36


(e)
ODPA-DPD
8.023 8.009 7.623 7.611 6.807 6.554 5.750 5.048
2.025 1.924
2.08 3.87 2.01 2.07 4.26 4.00 6.11 6.13

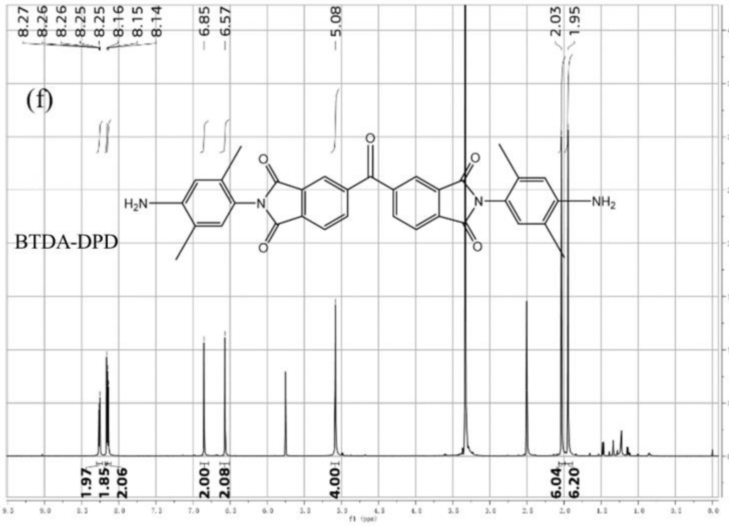


Figure S1. ^{1}H-NMR spectra of **FDA-DAT**、**ODPA-DAT**、**BTDA-DAT**、 **FDA-DPD**、**BTDA-DPD** in DMSO-d_6 and **ODPA-DPD** in $CDCl_3$.

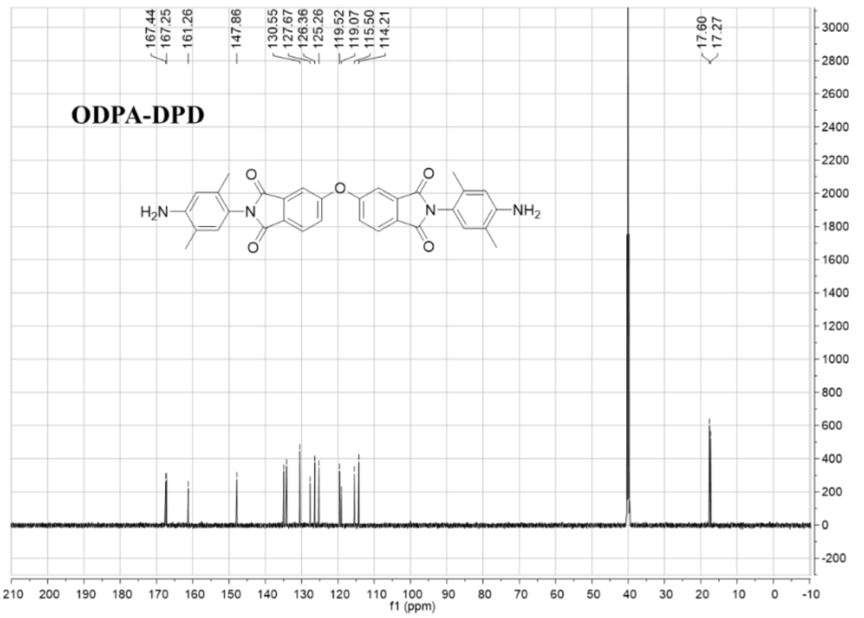


Figure S2. ^{13}C-NMR spectrum of **ODPA-DPD** in $CDCl_3$

2.2 FT-IR spectra of hybrid films and TPA

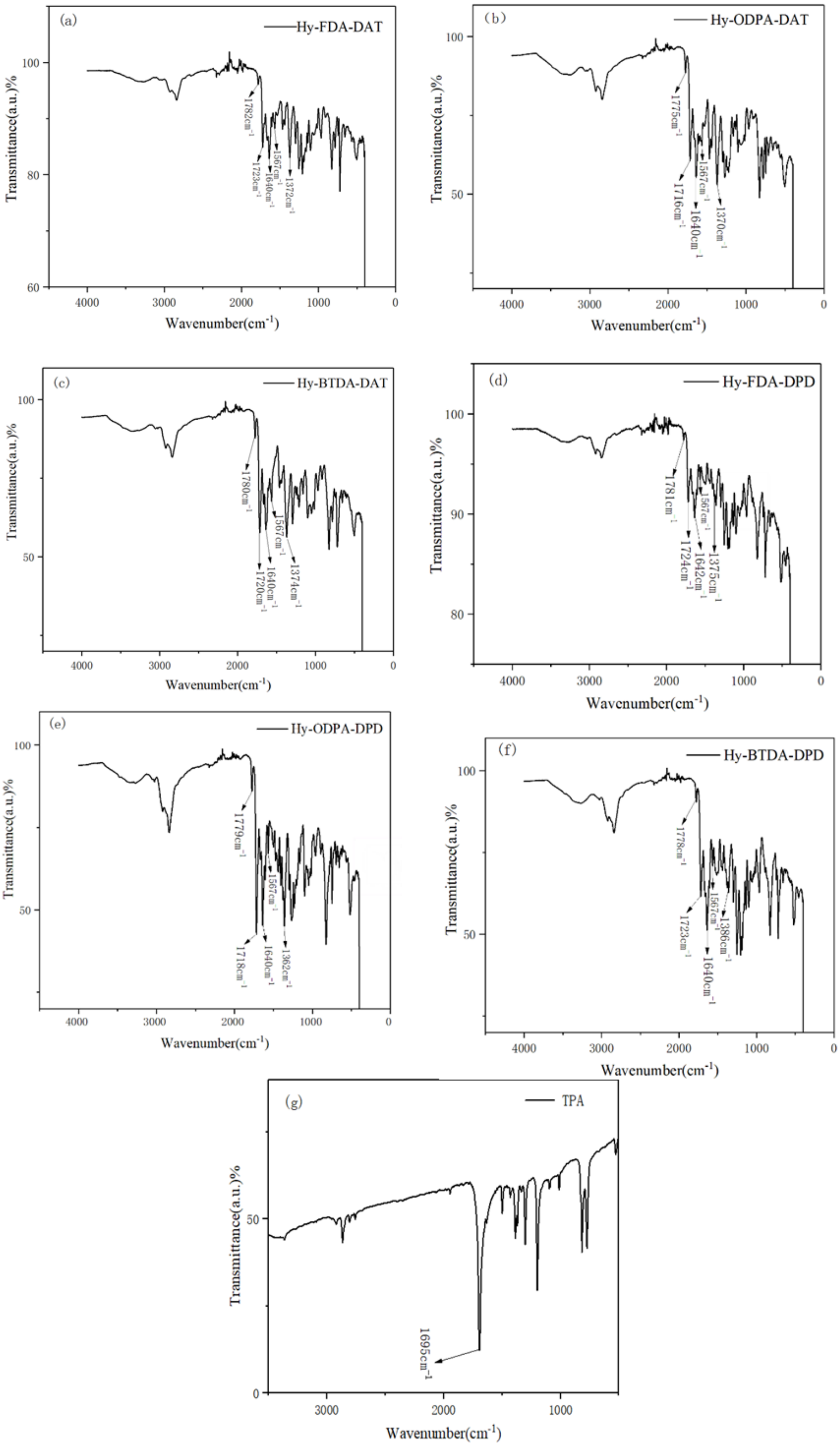
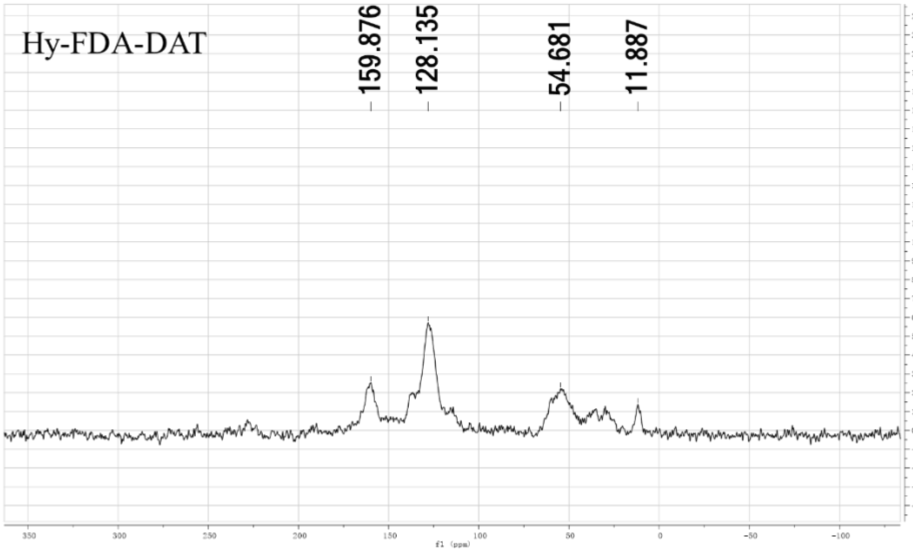
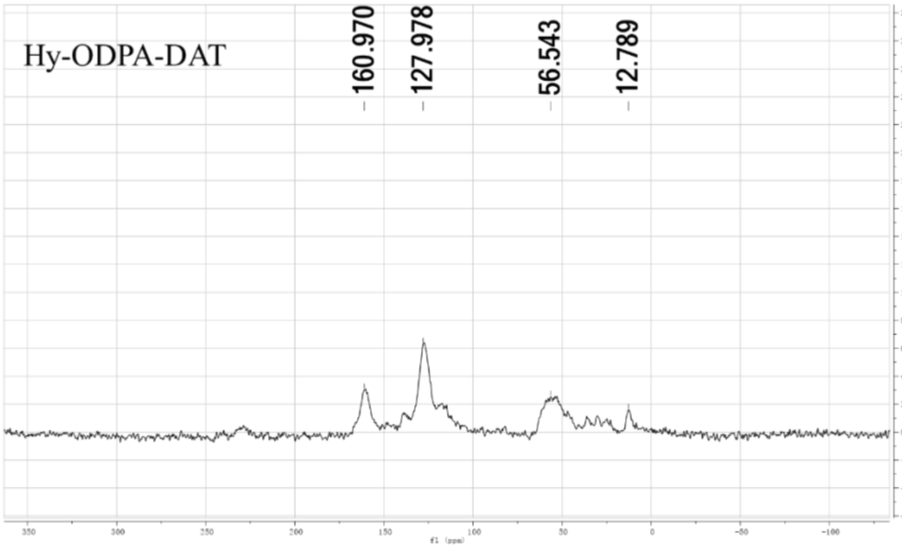
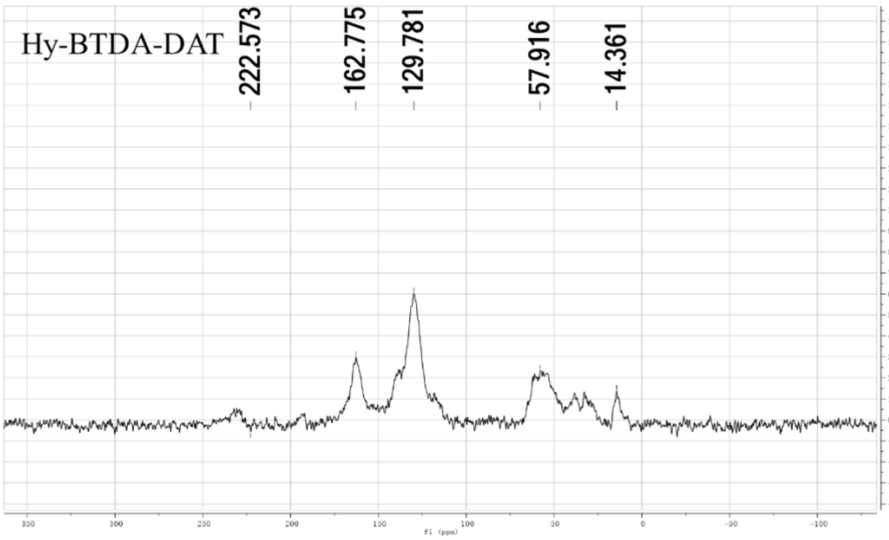


Figure S3 FT-IR spectra of Hy-FDA-DAT (a), Hy-ODPA-DAT (b), Hy-BTDA-DAT (c), Hy-FDA-DPD (d), Hy-ODPA-DPD (e), Hy-BTDA-DPD (f), and TPA (g).

2.3 Solid-state ^{13}C NMR spectra of hybrid materials







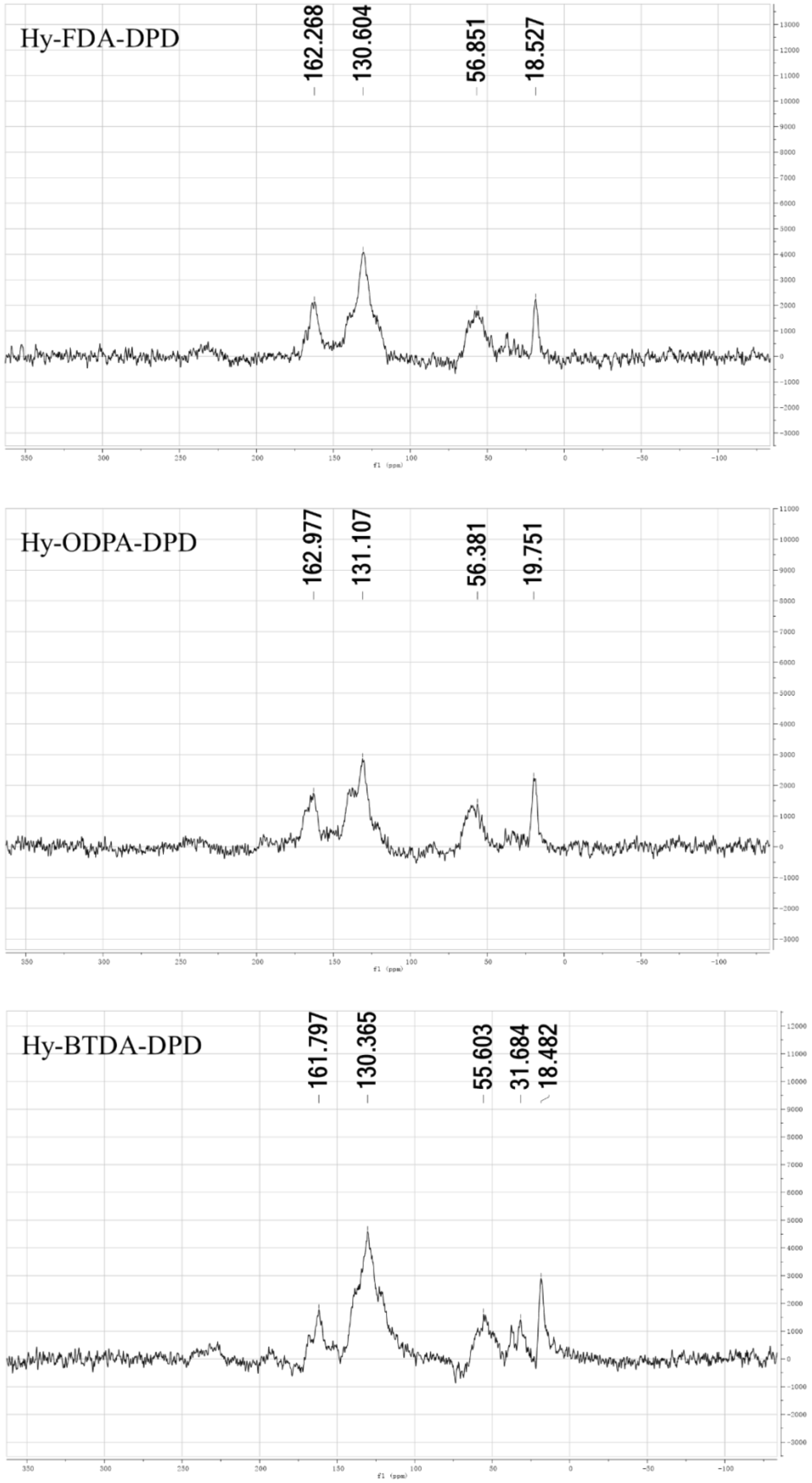


Figure S4 Solid-state ^{13}C-NMR spectra of PIm-PI powders.

2.4 Atomic force microscopy images of the hybrid films

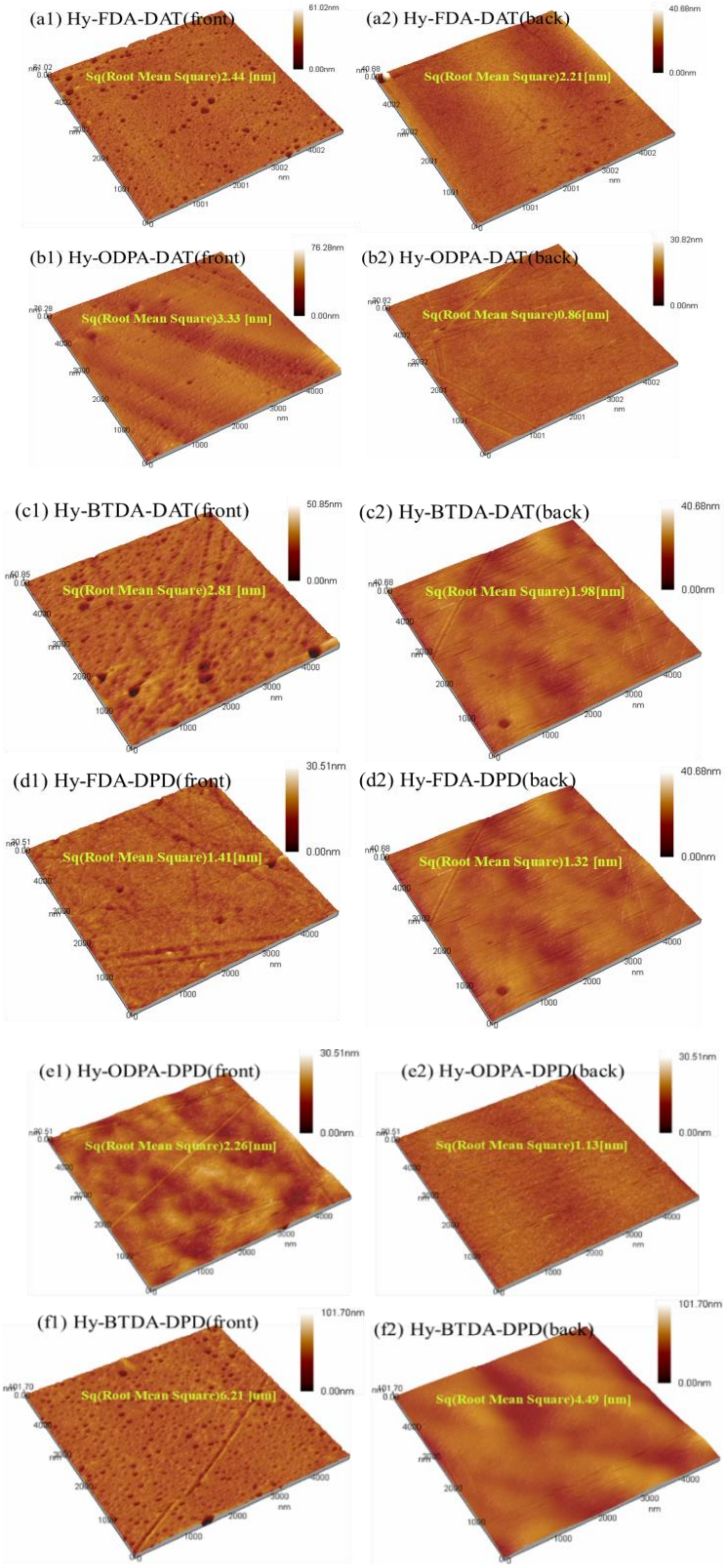


Figure S5 AFM images of PIm-PIs films (front: the top side in contact with air, back: the bottom side in contact with the glass dish of the film during the preparation).

2.5 Mechanical properties of the hybrid films

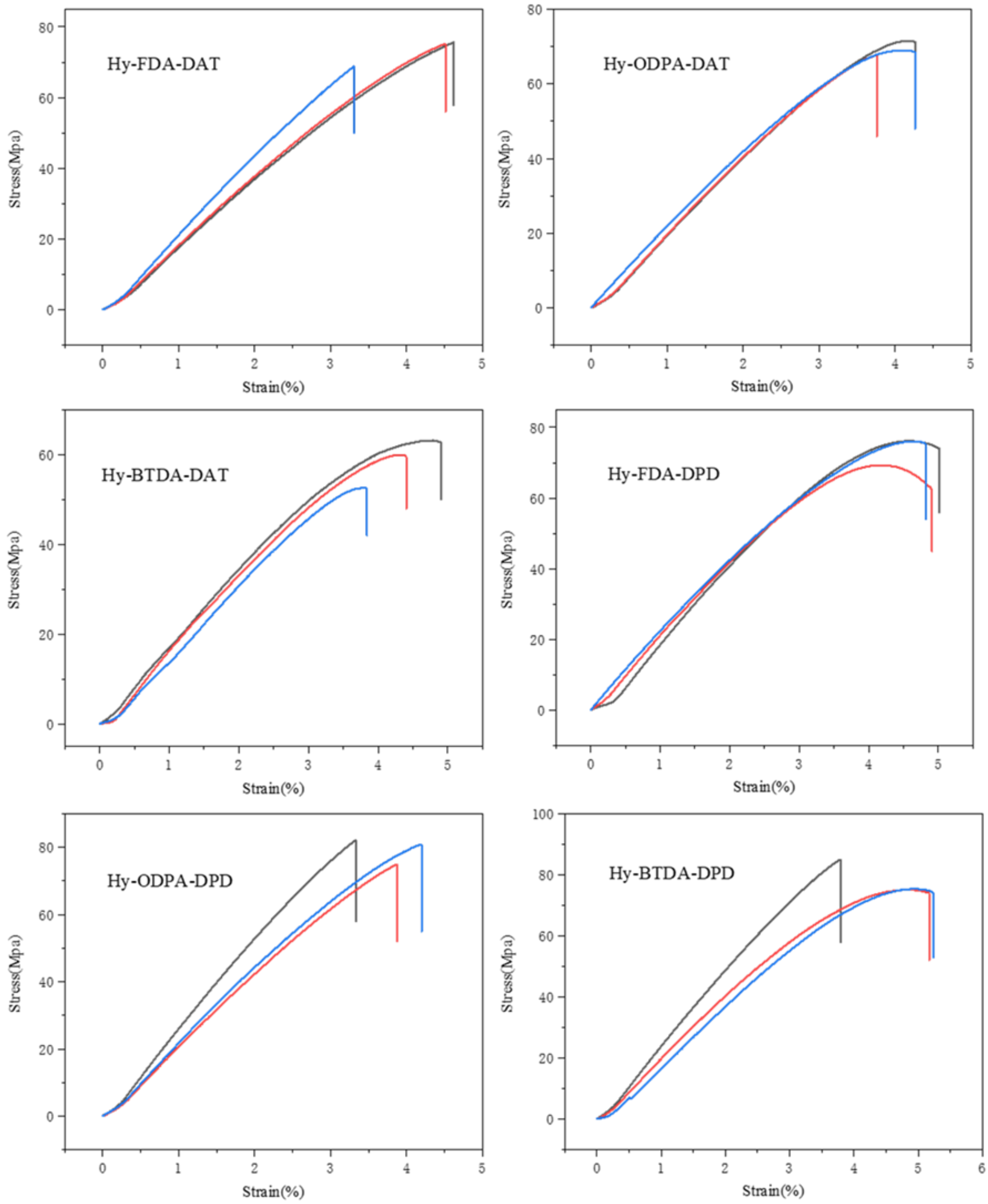


Figure S6 Tensile stress-strain curves of the as-synthesized hybrid films. Three different samples were tested for each material.

2.6 Dynamic mechanical analysis (DMA) of the hybrid films

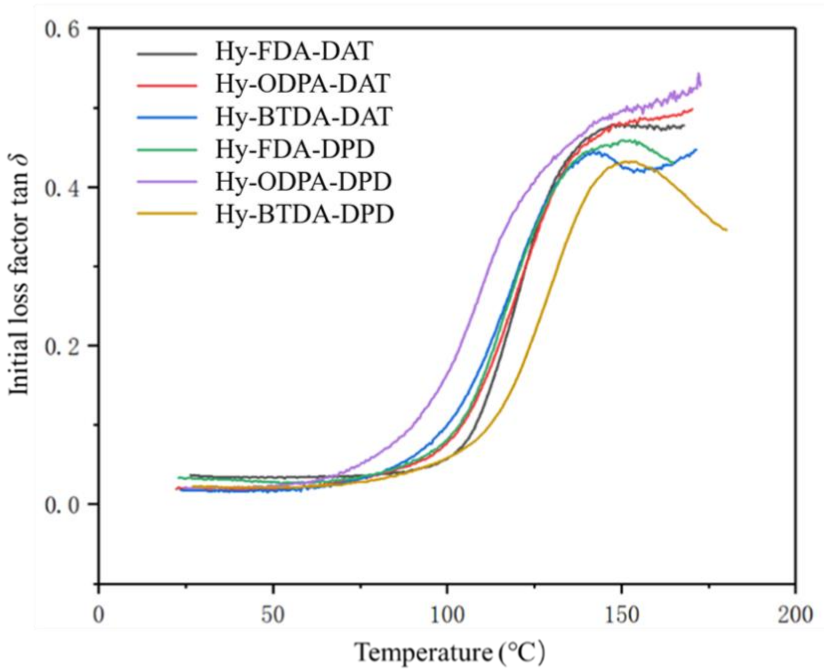


Figure S7 Initial loss factor tan δ curves of PIm-PIs films.

2.7 Thermal gravimetric analysis (TGA) of the hybrid films

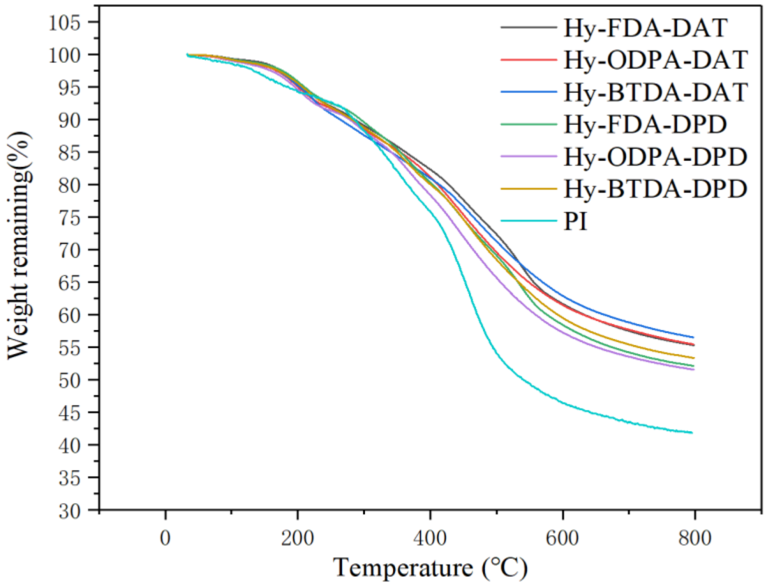


Figure S8 TGA curves of the PIm-PIs films and PI film

Table S1 TGA analysis of PIm-PIs and PI

materials	T_d 5%	T_d 10%	residue@600 ℃	residue@800 ℃
Hy-FDA-DAT	208 ℃	285 ℃	62%	55%
Hy-ODPA-DAT	200 ℃	279 ℃	62%	55%
Hy-BTDA-DAT	203 ℃	263 ℃	63%	56%
Hy-FDA-DPD	210 ℃	294 ℃	58%	52%
Hy-ODPA-DPD	196 ℃	277 ℃	57%	51%
Hy-BTDA-DPD	206 ℃	282 ℃	60%	53%
PI	187 ℃	286 ℃	46%	41%

3. Repairing of the hybrid films

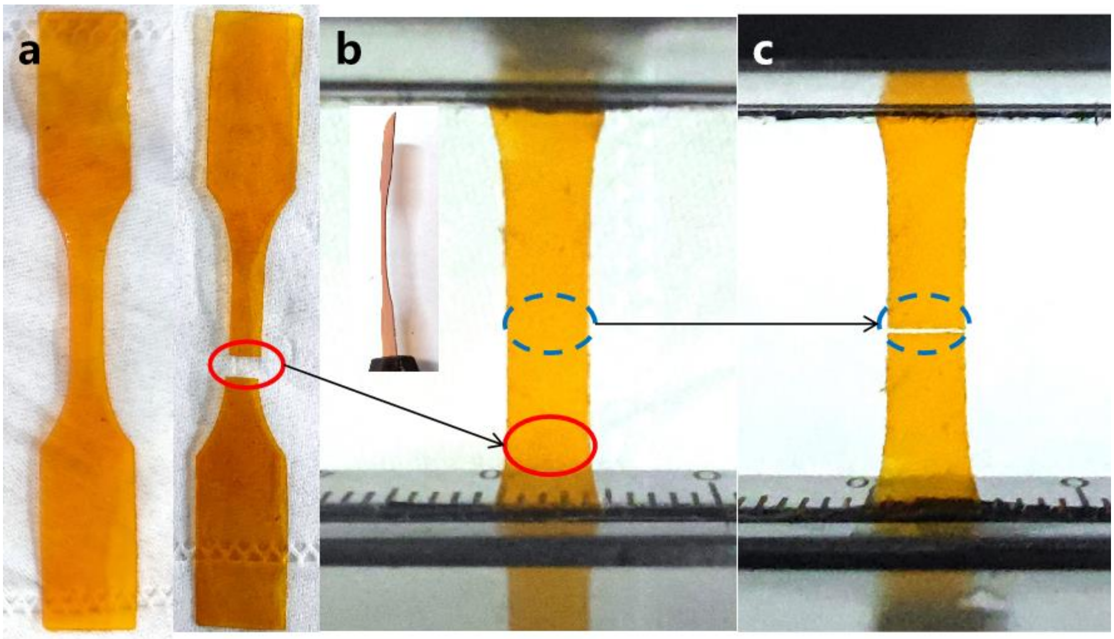


Figure S9 The optical images of the PIm-PI (Hy-ODPA-DAT) film before (a, left: as-synthesized, right: cut piece) and after heat-pressing (b), and after the second tensile testing (c). The rehealed positions are indicated by the red circles, and the dashed blue circles indicate the new fractured locations.

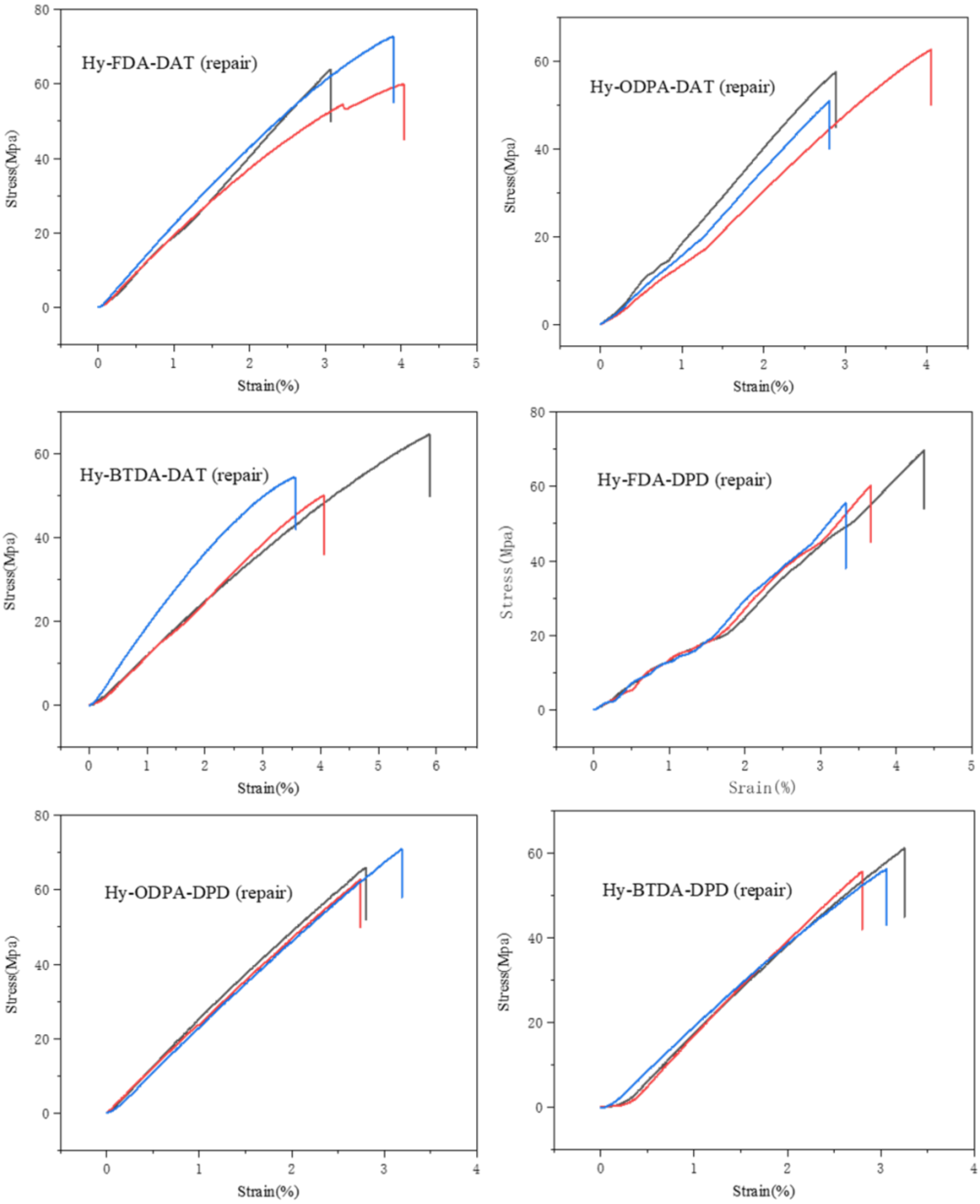


Figure S10 Tensile stress-strain curves of the as-synthesized hybrid films after repair. Three different samples were tested for each material.

Table S2 The mechanical properties of hybrid films before and after repair

Sample			Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)
Hy-FDA-DAT	original	average	2.1132±0.17	73.1964±3.10	4.1473±0.59
		01	1.9591	75.5832	4.6187
		02	2.0197	75.1916	4.5142
		03	2.3607	68.8143	3.3090
	repair	average	2.1376±0.14	65.496±5.36	3.6682±0.43
		01	2.2912	63.8864	3.0707
		02	1.9505	59.8862	4.036
		03	2.1711	72.7154	3.898
	Repair efficiency		101%	89%	88%
Hy-ODPA-DAT	original	average	2.1646±0.04	69.3695±1.64	4.0979±0.24
		01	2.1792	71.5577	4.2689
		02	2.2096	67.5944	3.7614
		03	2.1049	68.9565	4.2635
	repair	average	2.0250±0.19	56.9773±4.79	3.2474±0.57
		01	2.2766	57.4532	2.8837
		02	1.8011	62.5962	4.0546
		03	1.9974	50.8824	2.804
	Repair efficiency		94%	82%	79%
Hy-BTDA-DAT	original	average	1.7875±0.09	58.5119±4.51	4.3846±0.44
		01	1.6768	63.1792	4.9067
		02	1.8873	59.9501	4.406
		03	1.7985	52.4064	3.841
	repair	average	1.8873±0.38	56.3199±6.09	4.5056±0.99
		01	1.9052	54.3828	3.571
		02	2.3461	64.5549	5.8870
		03	1.4107	50.0221	4.059
	Repair efficiency		106%	96%	103%
Hy-FDA-DPD	original	average	2.2327±0.08	73.8496±3.20	4.9182±0.08
		01	2.3165	76.1634	5.019
		02	2.2637	69.3266	4.9121
		03	2.1180	76.0587	4.8236
	repair	average	2.1168±0.24	61.8471±4.02	3.7862±0.43
		01	2.0259	69.6602	4.3661
		02	2.1424	55.5794	3.3315
		03	2.1821	60.3017	3.6611
	Repair		95%	84%	77%

	efficiency				
Hy-ODPA-DPD	original	average	2.4939±0.23	79.2154±3.15	3.8017±0.36
		01	2.8126	82.1108	3.3311
		02	2.2631	74.8389	3.8749
		03	2.4061	80.6964	4.1991
	repair	average	2.4336±0.07	66.4677±3.38	2.9097±0.20
		02	2.5336	65.8388	2.8011
		03	2.3840	70.8872	3.189
		04	2.3831	62.6770	2.739
	Repair efficiency		98%	84%	77%
Hy-BTDA-DPD	original	average	2.2333±0.33	78.4486±4.55	4.7334±0.67
		01	2.6358	84.8812	3.7922
		02	1.8331	75.3615	5.236
		03	2.2310	75.1030	5.172
	repair	average	2.2258±0.09	57.6996±2.50	3.0387±0.19
		01	2.2415	61.2232	3.253
		02	2.3360	55.6425	2.7991
		03	2.1000	56.2330	3.064
	Repair efficiency		100%	74%	64%
PI	original	average	1.2196±0.07	36.8526±0.27	4.342±0.32
		01	1.1762	36.8552	4.353
		02	1.3197	36.5237	3.945
		03	1.1628	37.1789	4.728
	repair	average	1.2475±0.05	43.7047±1.56	4.3733±0.31
		01	1.2683	43.1827	4.404
		02	1.1806	45.8295	4.735
		03	1.2936	42.1019	3.981
	Repair efficiency		102%	119%	101%

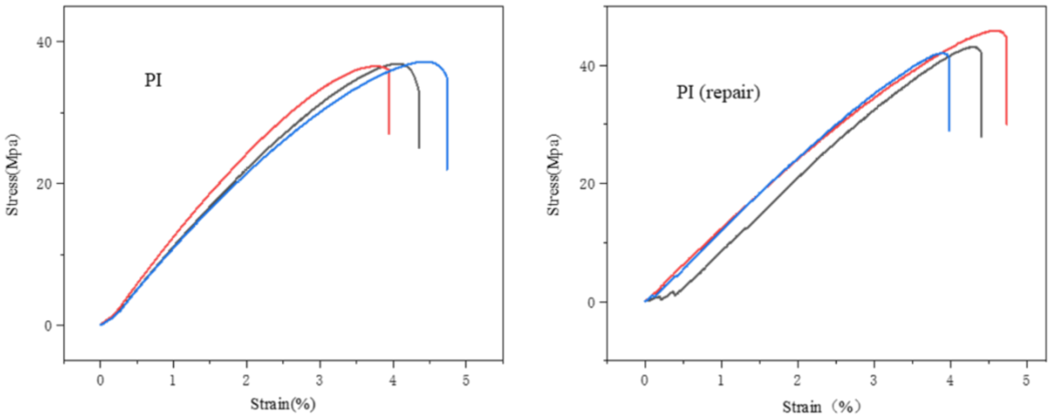


Figure S11 Tensile stress-strain curves of PI before and after repair. Three different samples were tested.

4. Recycling of the hybrid films

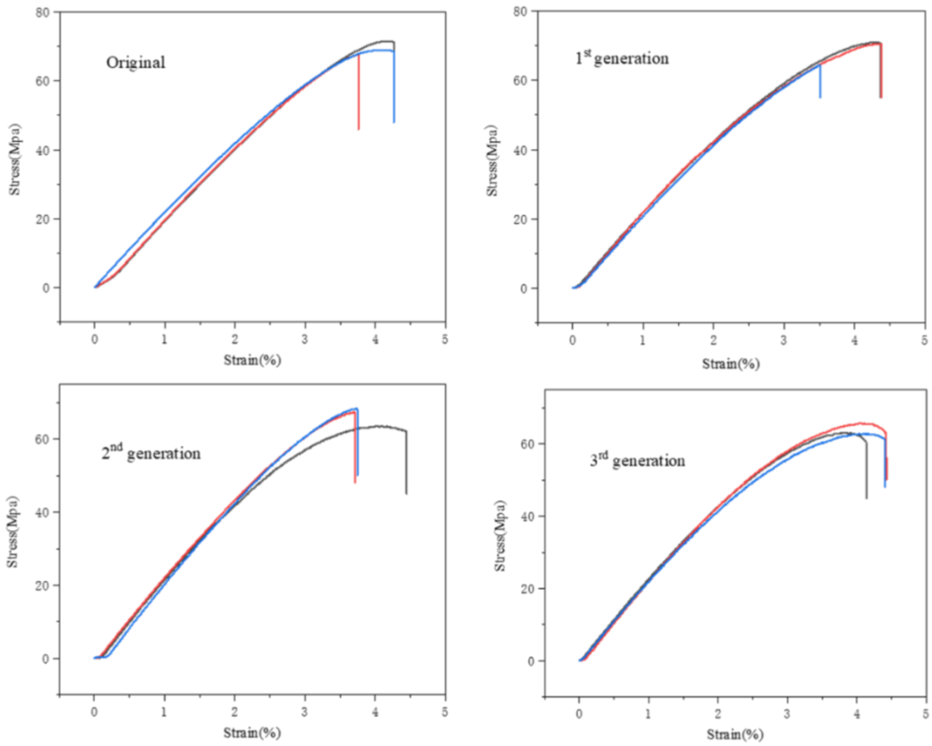


Figure S12 Tensile stress-strain curves of Hy-ODPA-DAT sample with three depolymerization-reformation process. Three different samples were tested for each material.

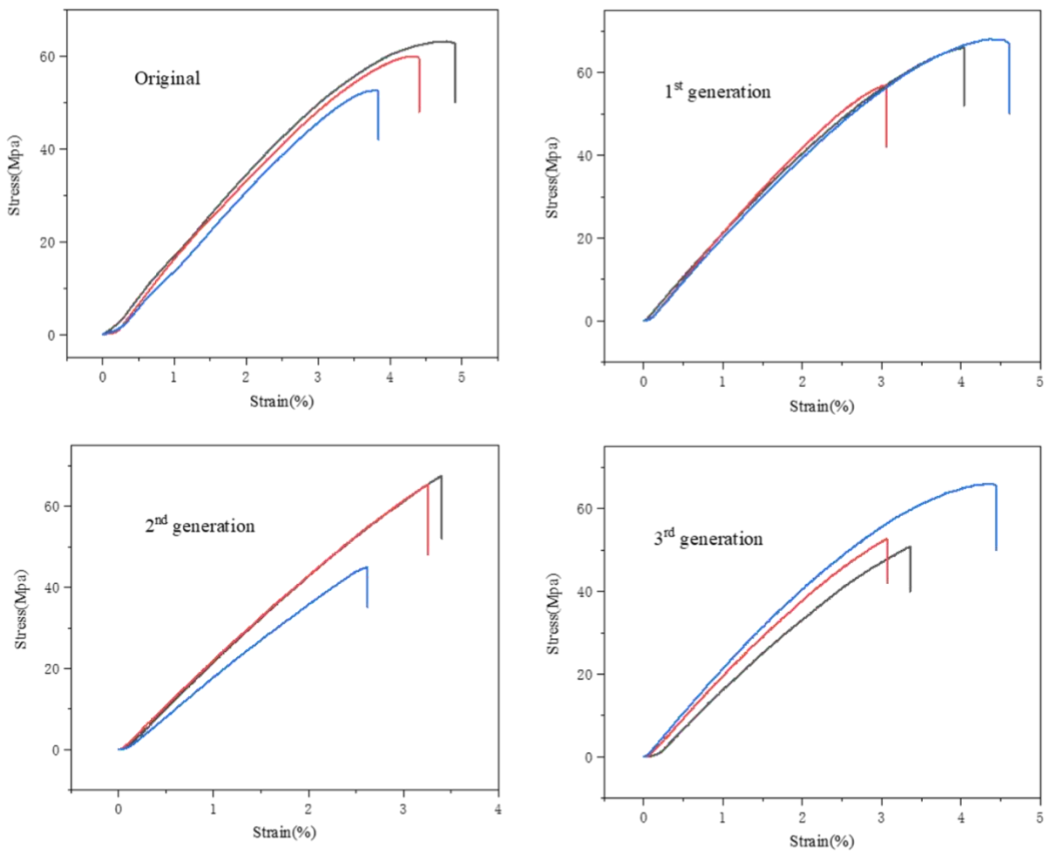


Figure S13 Tensile stress-strain curves of Hy-BTDA-DAT sample with three depolymerization-reformation process. Three different samples were tested for each material.

Table S3 The mechanical properties of Hy-ODPA-DAT and Hy-BTDA-DAT after 3 generation recycling.

Sample			Tensile Modulus (GPa)	Tensile Strength (MPa)	Elongation at break (%)
Hy-ODPA-DAT	original	average	2.1646±0.044	69.3695±1.644	4.0979±0.238
		01	2.1792	71.5577	4.2689
		02	2.2096	67.5944	3.7614
		03	2.1049	68.9565	4.2635
	1st generation	average	2.2013±0.026	68.5989±2.973	4.0844±0.407
		01	2.1794	70.9069	4.364
		02	2.2383	70.4892	4.381
		03	2.1862	64.4007	3.5082
	2nd generation	average	2.2768±0.071	66.3281±2.103	3.9667±0.339
		01	2.2298	63.4003	4.446
		02	2.3775	68.2449	3.745
		03	2.2231	67.3390	3.709
	3rd generation	average	2.2270±0.031	63.7695±1.311	4.3240±0.129
		01	2.2061	62.9560	4.1421
		02	2.2713	65.6203	4.424
		03	2.2036	62.7323	4.406
Hy-BTDA-DAT	original	average	1.7875±0.086	58.5119±4.514	4.3846±0.435
		01	1.6768	63.1792	4.9067
		02	1.8873	59.9501	4.406
		03	1.7985	52.4064	3.841
	1st generation	average	2.0868±0.073	63.6671±4.857	3.9023±0.641
		01	2.0949	66.0955	4.037
		02	2.1715	56.8889	3.059
		03	1.9940	68.0170	4.611
	2nd generation	average	2.1416±0.155	59.2366±10.140	3.094±0.339
		01	2.2738	67.4309	3.403
		02	2.2265	65.3306	3.257
		03	1.9246	44.9482	2.621
	3rd generation	average	1.9798±0.147	56.4484±6.762	3.622±0.590
		01	1.7817	50.7321	3.359
		02	2.0235	52.6669	3.068
		03	2.1343	65.9461	4.439