

Supporting Information

Synthesis of epoxidized-poly(ester carbonate)-*b*-polyimide-*b*-poly(ester carbonate): reactive single-wall carbon nanotube dispersants enable synergistic reinforcement around multi-wall nanotube grafted carbon fibers†

Bo Liu^{a‡}, Chengyin Liu^{a‡}, Hugo G. De Luca^{b‡}, Suresh Kumar Raman Pillai^{a‡}, David B. Anthony^c, Jianghua Li^a, Alexander Bismarck^c, Milo S.P. Shaffer^{b,d*} and Mary B. Chan-Park^{a*}

Table S1 Synthesized PMACEP-PI-PMACEP (TB3a, TB3b) from PMAC-PI-PMAC (TB2a, TB2b).

Table S2 Solubility of TBs in common solvents.

Table S3 Raman data of pristine SWNTs and TB/SWNTs.

Table S4 Mechanical Properties of neat EP and SWNT/TB/EP Composite Films with standard deviation along with maximum and minimum is provided.

Table S5 Mechanical properties of single fiber pull-out tests with neat and TB3b-dispersed SWNTs reinforced epoxy matrix.

Figure S1 ¹H NMR spectrum of OH-PI-OH (*d*₆-DSMO, 25 °C).

Figure S2 ¹H NMR spectrum of TB1a (*d*₆-DSMO, 25 °C) (*: DMAc residue).

Figure S3 ¹H NMR spectrum of TB1b (*d*₆-DSMO, 25 °C) (*: DMAc residue).

Figure S4 ¹H NMR spectrum of TB2a (*d*₆-DSMO, 25 °C).

Figure S5 ¹H NMR spectrum of TB2b (*d*₆-DSMO, 25 °C).

Figure S6 ¹H NMR spectrum of TB3a (*d*₆-DSMO, 25 °C).

Figure S7 ¹H NMR spectrum of TB3b (*d*₆-DSMO, 25 °C).

Figure S8 GPC curves of OH-PI-OH, PLA-PI-PLA (TB1a, TB1b), PMAC-PI-PMAC (TB2a, TB2b) and PMACEP-PI-PMACEP (TB3a, TB3b) (full-range of the retention time).

Figure S9 Visual appearance of SWNT/TB/epoxy composite films (a) 0.5 wt.% SWNTs (b) 1 wt.% SWNTs (c) 2 wt.% SWNTs dispersed with(i) TB1b (ii) TB2b (iii) TB3b.

Figure S10 Average apparent interfacial shear strength given by the gradient of linear fit (red line) when peak force is plotted as a function of embedded area for (a) unsized carbon fibers and (b) CNT-g-CFs in neat epoxy, (c) unsized carbon fibers and (d) CNT-g-CFs in TB3b-dispersed SWNTs (0.1 wt.%) reinforced epoxy, (e) unsized carbon fibers and (f) CNT-g-CFs in TB3b-dispersed SWNTs (1.0 wt.%) reinforced epoxy.

Figure S11 ¹H NMR spectrum of MAC (CDCl₃, 300M, 25 °C).

Figure S12 Schematic representation of the single fiber pull-out test equipment.

Table S1 Synthesized PMACEP-PI-PMACEP (TB3a, TB3b) from PMAC-PI-PMAC (TB2a, TB2b).

Sample	Design [<i>m</i> -CPBA]:[ene] ^a /Actual Ratios of alkene and epoxy	TB measured M _n (Da) ^b
TB3a	1:2/1:1	11100
TB3b	1:2/3:1	15300

^a Mole ratio of m-CPBA and alkene groups in TB2a and TB2b.^b Determined from GPC using polystyrene standards as references.**Table S2** Solubility of TBs in the common solvents.

Sample	Solubility				
	NMP	DMF	THF	MeOH	water
TB1b	+	+	+	-	-
TB2b	+	+	+	-	-
TB3b	+	+	+	-	-

+, good solubility; -, insoluble after 30min

Table S3 Raman data of as-received (pristine) SWNTs and TB/SWNTs.

Sample	I _D	I _G	I _D /I _G	RBM peaks (cm ⁻¹)	G band peaks (cm ⁻¹)	2D band peaks (cm ⁻¹)
SWNTs	2039.1	29159.3	0.070	149.3/164.8	1590.9	2628.8
TB1a/SWNTs	2439.2	57245.7	0.043	156.7/173.8	1592.0	2637.5
TB1b/SWNTs	3638.4	76024.1	0.048	156.7/173.8	1592.0	2636.6
TB2a/SWNTs	2732.5	55557.4	0.049	156.7/173.8	1592.0	2635.8
TB2b/SWNTs	3080.5	59194.3	0.052	156.7/173.8	1592.0	2634.9
TB3a/SWNTs	2402.2	59394.9	0.040	156.7/173.8	1592.0	2638.4
TB3b/SWNTs	2957.8	58997.1	0.050	156.7/173.8	1592.0	2636.6

Table S4 Mechanical Properties of neat EP and SWNT/TB/EP Composite Films with standard deviation along with maximum and minimum is provided.

No.	Sample	Strength		Modulus (GPa) Avg. (max, min)	Elongation at maximum stress (%) Avg. (max, min)
		(MPa) Avg. (max, min)			
1	Neat EP	47.8±4.2 (52.2,42.5)	1.9±0.2 (2.1,1.7)	4.19±0.75 (4.93,3.33)	
2	TB1b(2 wt.%)/EP	53.5±7.4 (61.1,39.2)	2.5±0.4 (3.0,1.9)	3.31±0.81 (4.28,2.11)	
3	TB2b(2 wt.%)/EP	45.1±4.4 (49.8,40.1)	2.3±0.3 (2.7,1.9)	2.84±0.29 (3.34,2.60)	
4	TB3b(2 wt.%)/EP	50.1±5.4 (60.5,47.7)	2.3±0.2 (2.4,1.9)	3.26±0.45 (4.20,2.98)	
5	SWNTs(1 wt.%)/TB1b/EP	63.3±4.1 (68.2,56.9)	2.6±0.4 (3.0,2.1)	4.79±0.80 (6.18,3.91)	
6	SWNTs(1 wt.%)/TB2b/EP	61.2±5.5 (66.8,53.5)	2.1±0.2 (2.3,1.8)	5.16±0.46 (5.55,4.36)	
7	SWNTs(1 wt.%)/TB3b/EP	60.3±2.2 (63.7,57.9)	2.1±0.3 (2.7,1.7)	5.82±1.12 (7.12,4.52)	
8	SWNTs(2 wt.%)/TB1b/EP	13.6±1.7 (16.1,11.9)	0.5±0.09 (0.6,0.3)	4.43±1.59 (7.66,3.05)	
9	SWNTs(2 wt.%)/TB2b/EP	55.1±4.4 (63.7,50.0)	2.2±0.3 (2.7,1.8)	5.29±1.45 (7.50,3.79)	
10	SWNTs(2 wt.%)/TB3b/EP	66.9±2.8 (69.9,62.6)	2.6±0.4 (3.5,2.0)	5.26±1.08 (6.86,3.68)	

Table S5 Mechanical properties of single fiber pull-out tests with neat and TB3b-dispersed SWNTs reinforced epoxy matrix.

Fiber	SWNT loading in epoxy (wt.%)	Average fibre diameter ^a (μm)	Number of specimens	Interfacial shear strength ^b (MPa)
As-received unsized carbon fiber	0	7.0 ± 0.3	14	89.4 ± 1.3
CNT-g-CF	0	6.8 ± 0.4	12	96.7 ± 2.3
As-received unsized carbon fiber	0.1	6.7 ± 0.4	9	90.7 ± 3.0
CNT-g-CF	0.1	6.8 ± 0.5	14	97.9 ± 2.2
As-received unsized carbon fiber	1.0	7.0 ± 0.3	10	95.6 ± 2.7
CNT-g-CF	1.0	7.0 ± 0.5	10	100.2 ± 1.5

^a Average fiber diameter from SEM after pull-out with standard deviation;

^b interfacial shear strength with standard error.

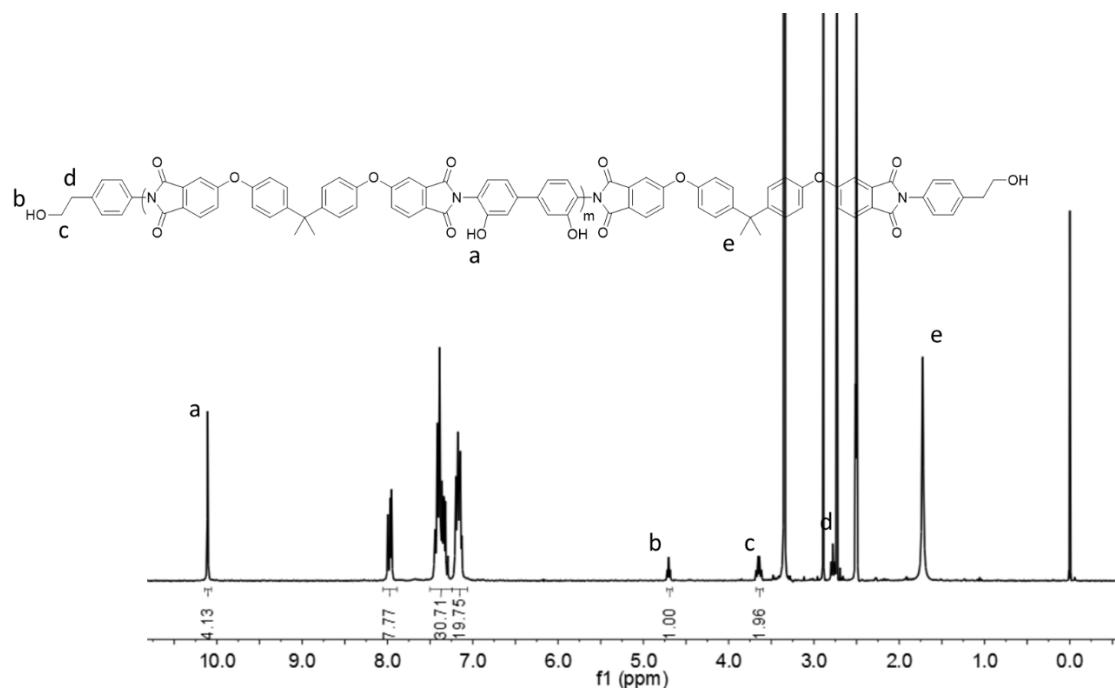


Figure S1 ^1H NMR spectrum of OH-PI-OH (d_6 -DSMO, 25 °C).

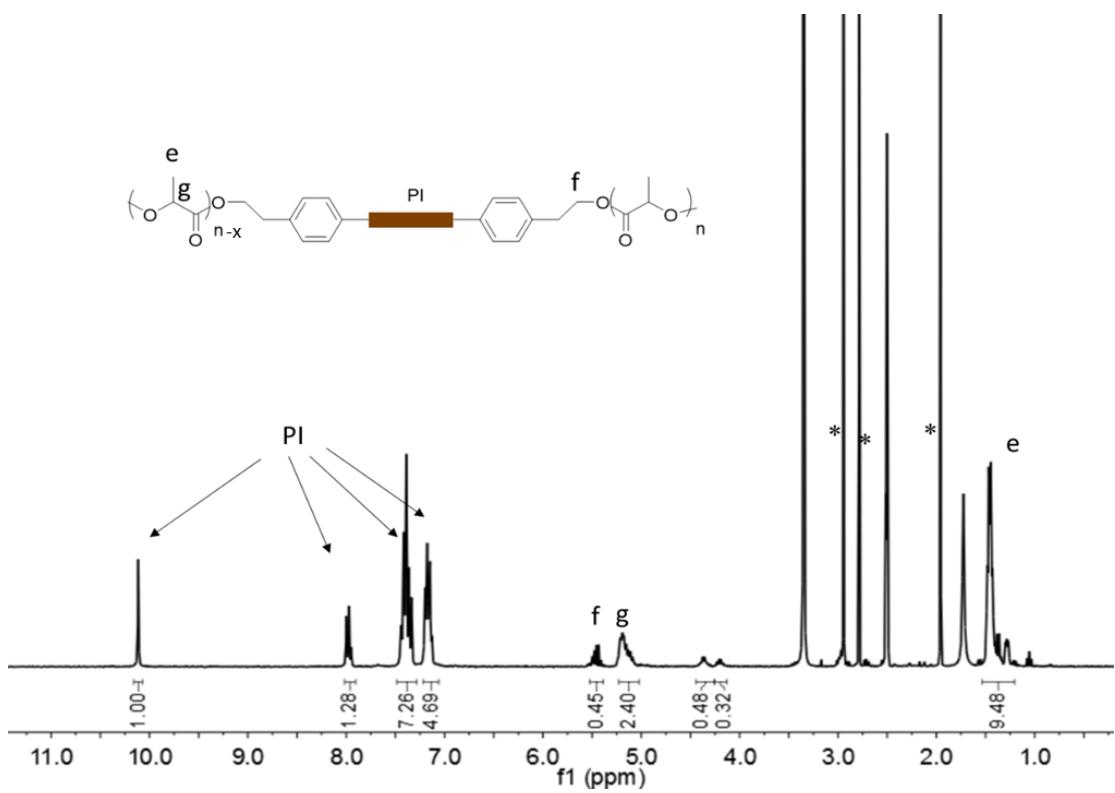


Figure S2 ^1H NMR spectrum of TB1a (d_6 -DSMO, 25 °C) (*: DMAc residue).

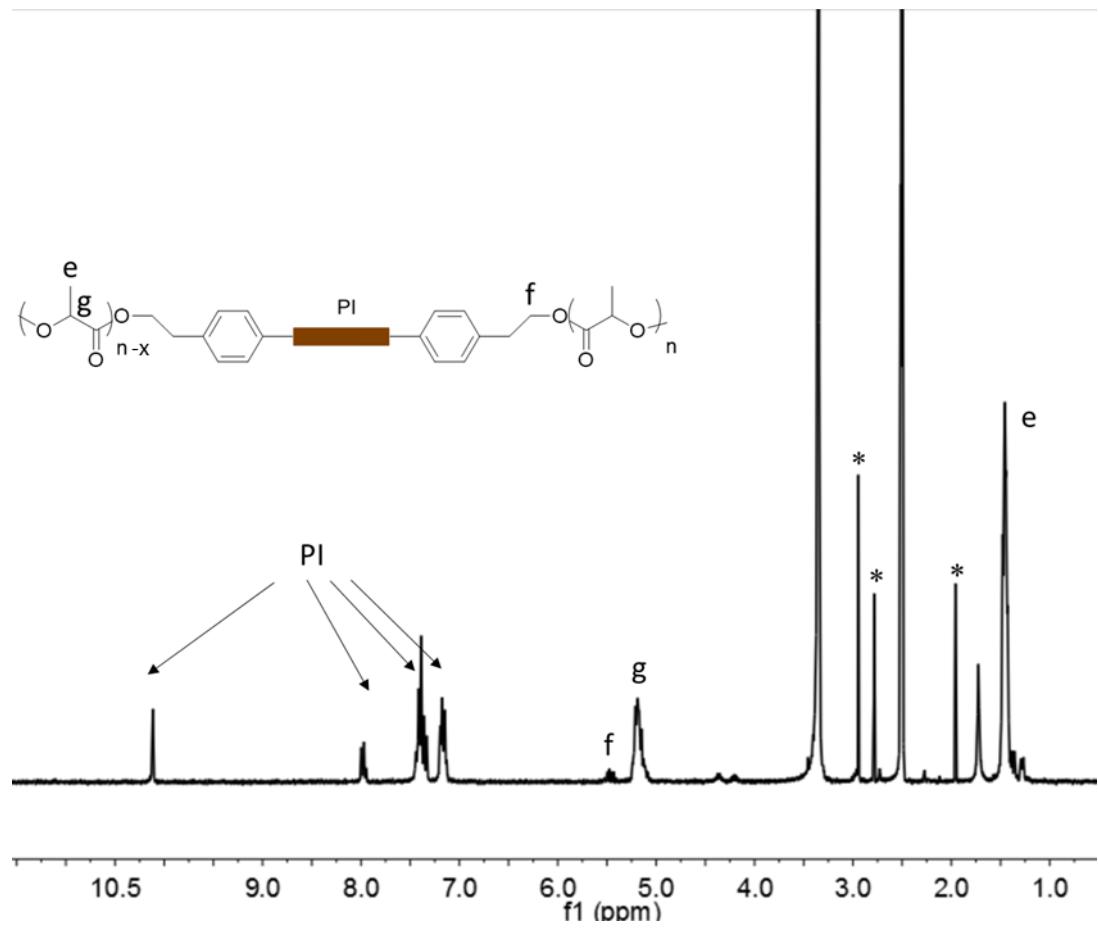


Figure S3 ^1H NMR spectrum of TB1b (d_6 -DSMO, 25 °C) (*: DMAc residue).

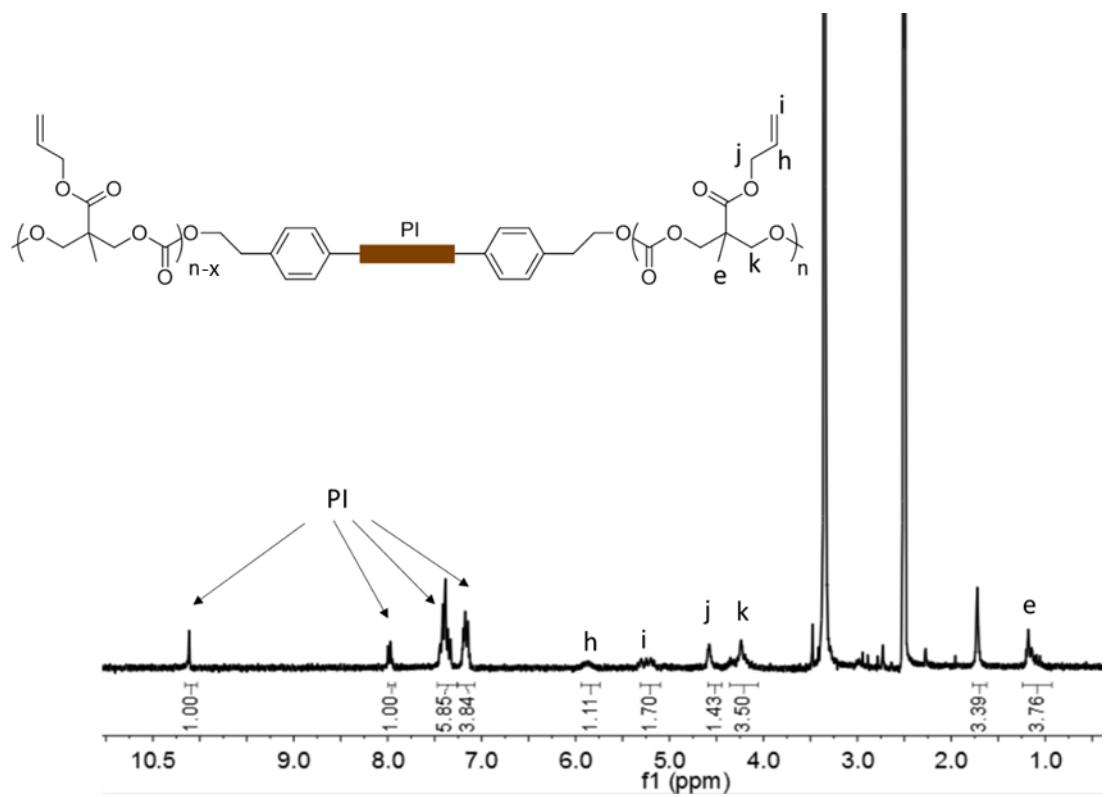


Figure S4 ^1H NMR spectrum of TB2a (d_6 -DSMO, 25 °C).

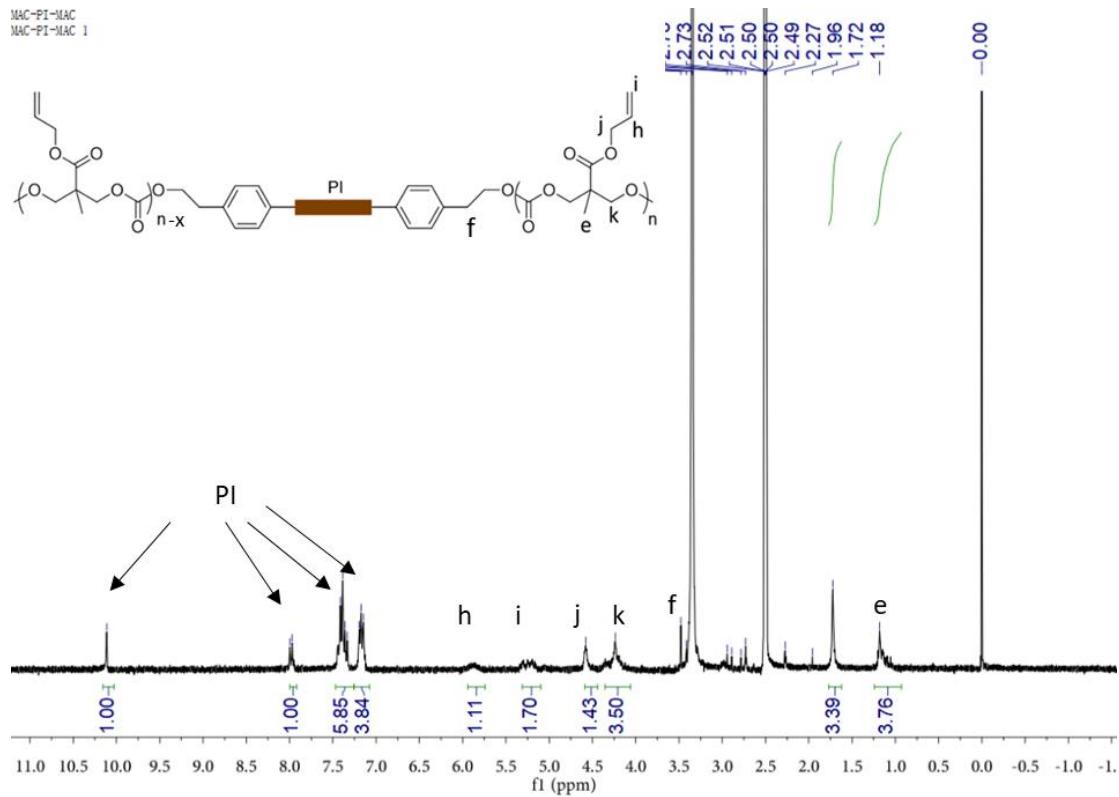


Figure S5 ^1H NMR spectrum of TB2b (d_6 -DSMO, 25 °C).

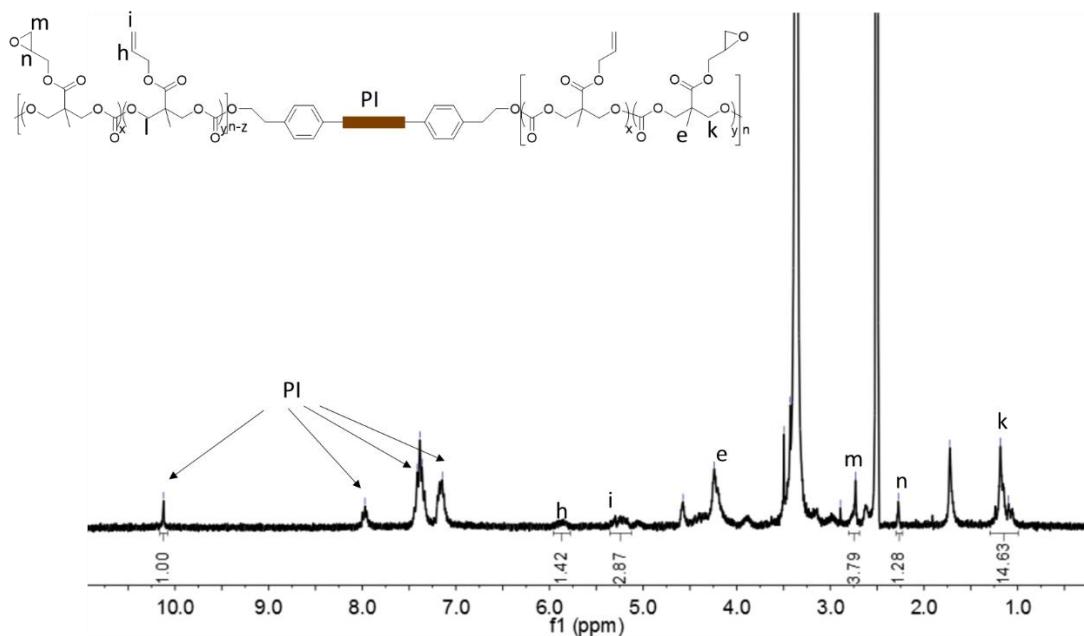


Figure S6 ^1H NMR spectrum of TB3a (d_6 -DSMO, 25 °C).

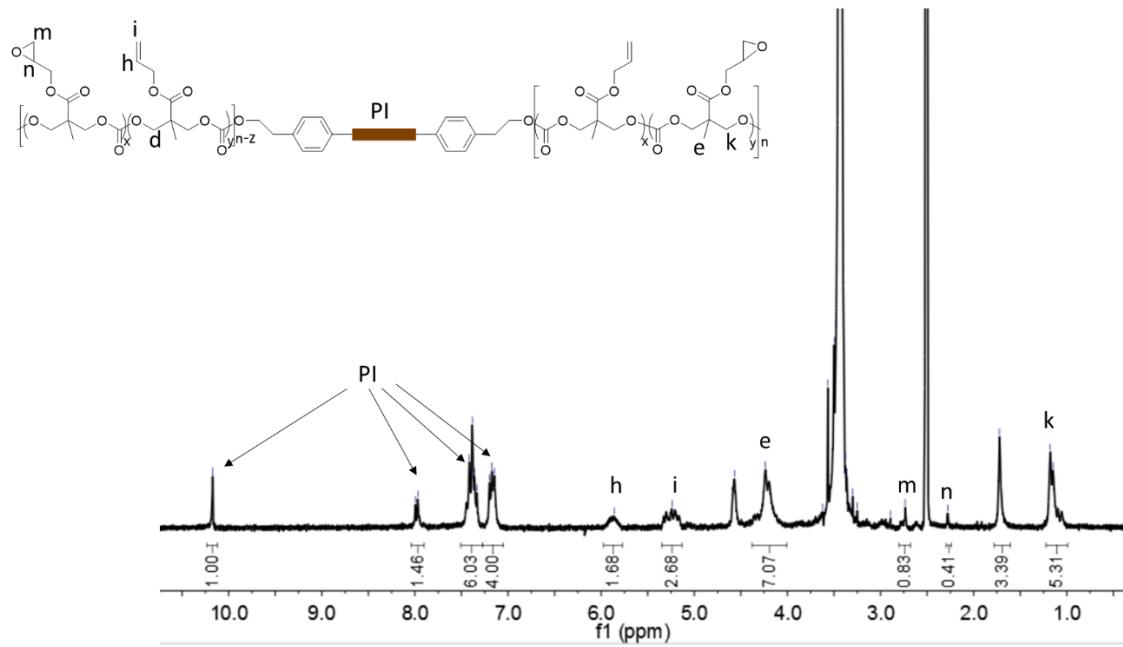


Figure S7 ¹H NMR spectrum of TB3b (*d*₆-DSMO, 25 °C).

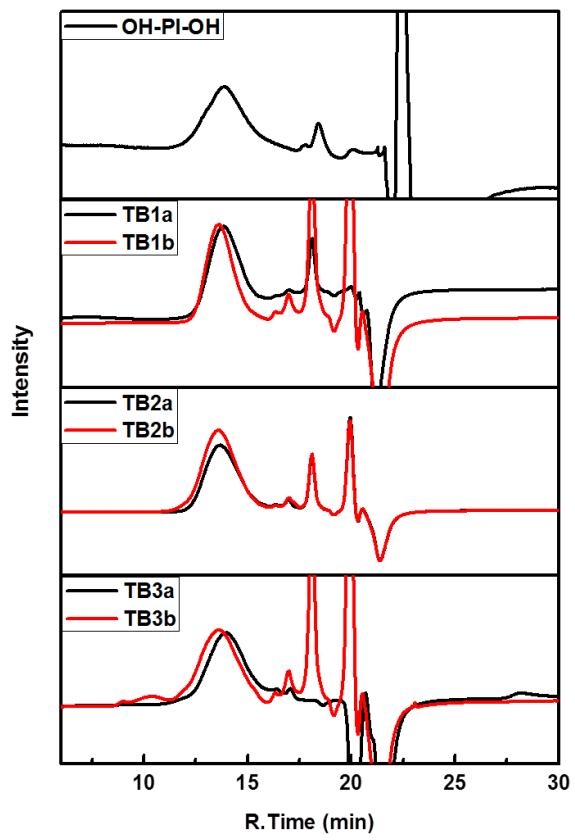


Figure S8 GPC curves of OH-PI-OH, PLA-PI-PLA (TB1a, TB1b), PMAC-PI-PMAC (TB2a, TB2b) and PMACEP-PI-PMACEP (TB3a, TB3b) (full-range of the retention time).

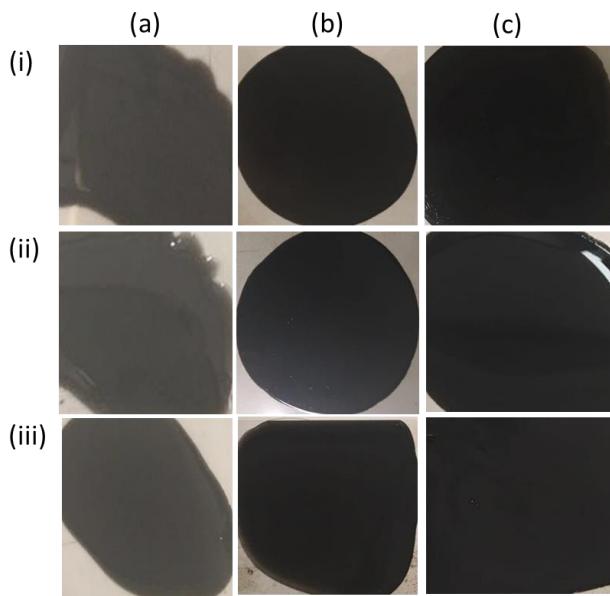


Figure S9 Visual appearance of SWNT/TB/epoxy composite films (a) 0.5 wt.% SWNTs (b) 1 wt.% SWNTs (c) 2 wt.% SWNTs dispersed with (i) TB1b (ii) TB2b (iii) TB3b.

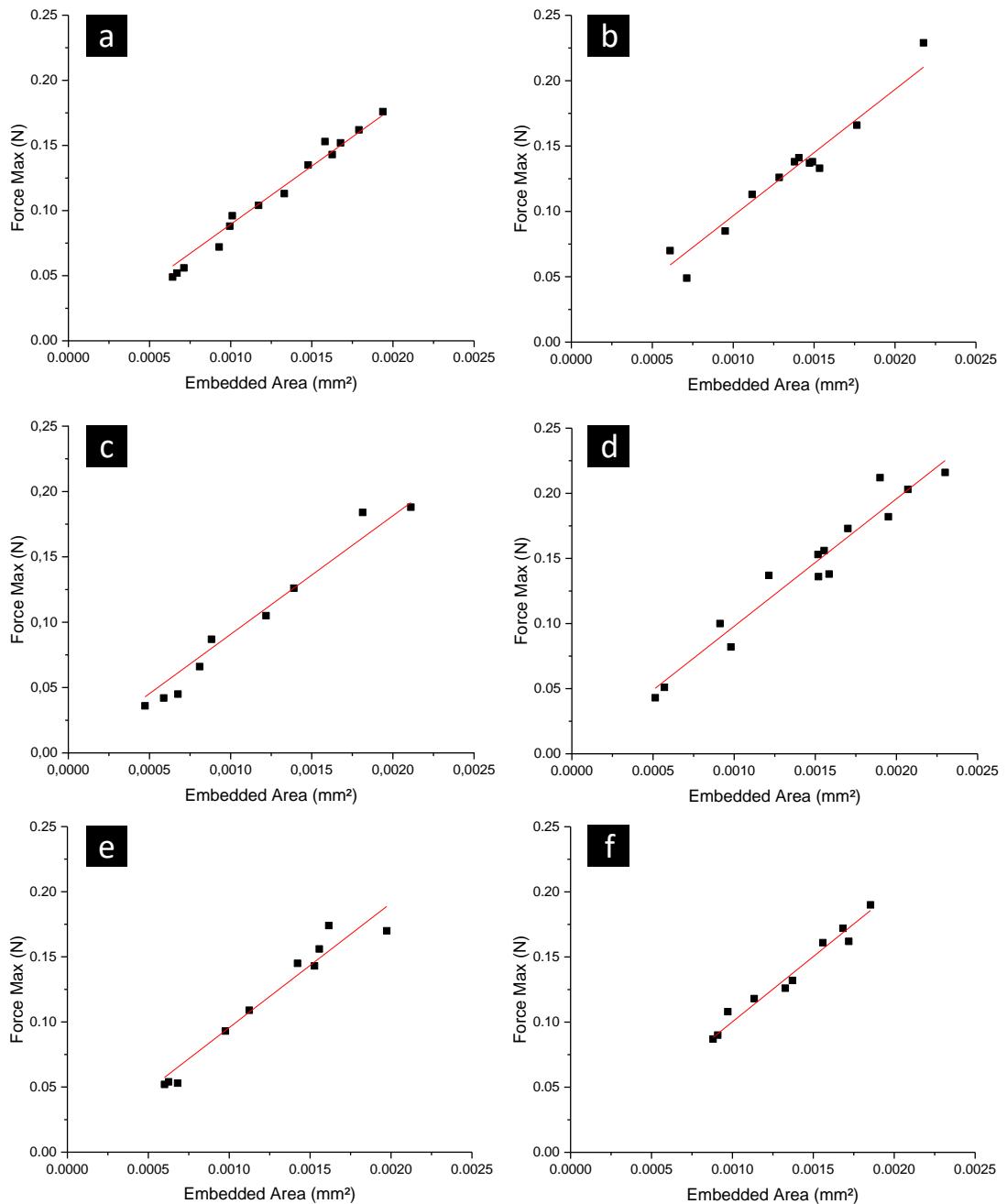


Figure S10 Average apparent interfacial shear strength given by the gradient of linear fit (red line) when peak force is plotted as a function of embedded area for (a) unsized carbon fibers and (b) CNT-g-CFs in neat epoxy, (c) unsized carbon fibers and (d) CNT-g-CFs in TB3b-dispersed SWNTs (0.1 wt.%) reinforced epoxy, (e) unsized carbon fibers and (f) CNT-g-CFs in TB3b-dispersed SWNTs (1.0 wt.%) reinforced epoxy.

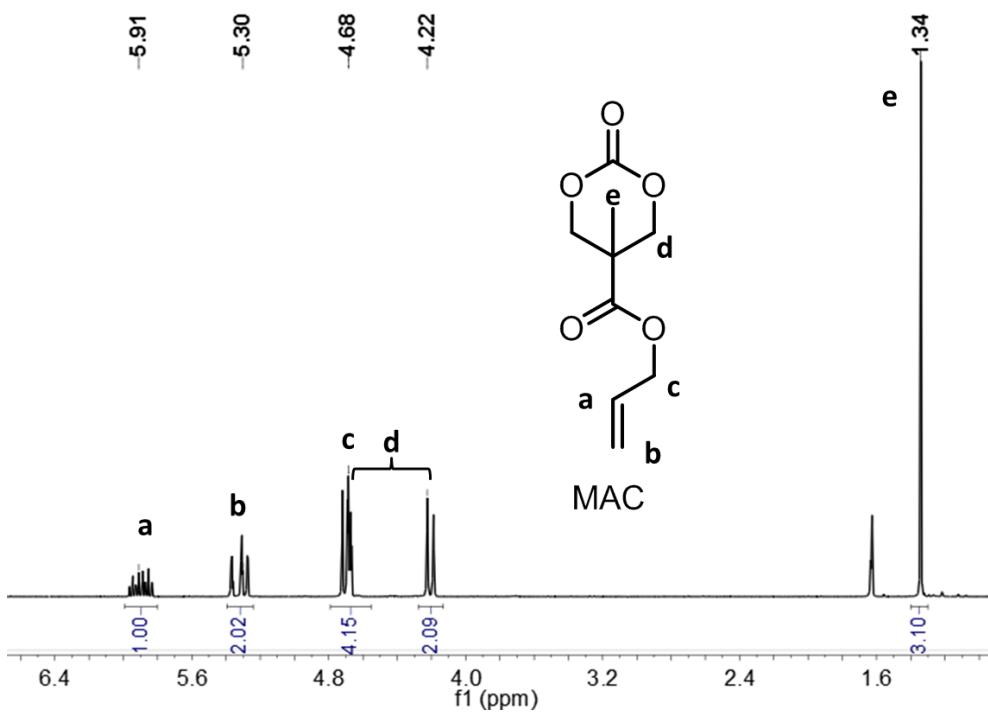


Figure S11 ^1H NMR spectrum of MAC (CDCl_3 , 300M, 25 °C).

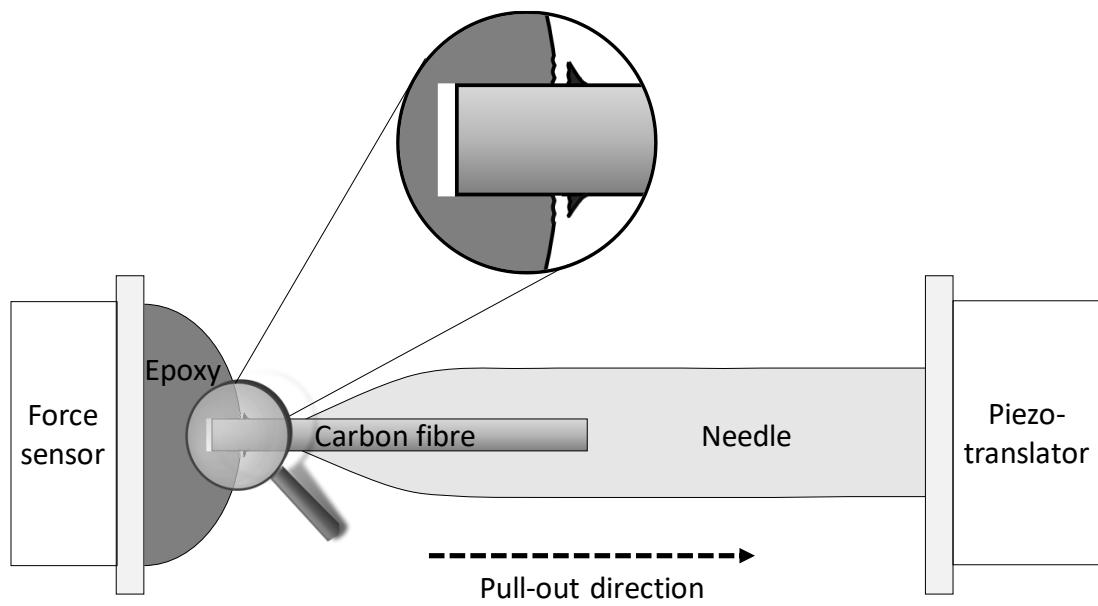


Figure S12 Schematic representation of the single fiber pull-out test equipment.