Supporting Information

Synchronously Enhanced Flame Retardance and Mechanical Properties Epoxy/Carbon Fiber Composites Achieved by Interfacial Structure Design†

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1. Experimental section

● Note S1

Preparation method of C@H: 0.8 g of OCF and 0.88 g of HCCP were added to a pressure resistant reactor containing 80 mL of anhydrous acetonitrile. After magnetic stirring at 25 °C for 10 min, the mixture was ultrasonicated for 5 min to enhance HCCP dispersion. Then, 5.2 mL of TEA was injected, and the reaction continued under nitrogen at 40 °C with stirring for 3 h. Finally, the fibers were filtered, washed, and dried to obtain the modified fibers named C@H.

Preparation method of C@HB: For the preparation of C@HB fibers, the initial steps were the same as those for C@H fibers. After the reaction with TEA, 3.12 g of BPS was added to the system, and the reaction continued for an additional 3 h. The fibers were then filtered, washed, and dried to obtain the modified fibers named C@HB.

Preparation method of PZS particles: 1.44 g of HCCP and 3.12 g of BPS were dissolved in 40 mL of anhydrous acetonitrile respectively. The solutions were magnetically stirred at room temperature for 10 min and then underwent ultrasonic treatment for 5 min to promote the dispersion of HCCP and BPS. Subsequently, the two solutions were mixed and stirred at 40 °C for 5 h. After the reaction was completed, the mixture was vacuum-filtered, and the reaction products were repeatedly washed with anhydrous ethanol and deionized water in an ultrasonic cleaner with an ultrasonic power of 60 watts to remove unreacted monomers and by-products. The modified carbon fibers were dried with a freeze dryer.

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Preparation method of E/C/P/6D composite: 1.25 g of PZS (The approximate amount of PZS on the CF surface was calculated from the thermogravimetric analysis (TGA) test results of the C@P-18 sample.) and 3.75 g of CF were added to a certain volume of anhydrous ethanol. The subsequent work for preparing the composite was completed based on the exactly same operation procedures for E/C@P-18/D samples.

● Supplementary tables

Table S1. The composition of relevant composites.

Samples	CF (g)	C@P-x-y (g)	Epoxy (g)	DDM (g)	DOPO (g)	PZS (g)
E/C	5	/	35.2	9.8	/	/
E/C/3D	5	/	34	9.5	1.5	/
E/C/6D	5	/	32.8	9.2	3	/
E/C/P/6D	3.75	/	32.8	9.2	3	1.25
E/C@P-7-5	/	5	35.2	9.8	/	/
E/C@P-11-5	/	5	35.2	9.8	/	/
E/C@P-18-5	/	5	35.2	9.8	/	/
E/C@P-23-5	/	5	35.2	9.8	/	/
E/C@P-18-5/3D	/	5	34	9.5	1.5	/
E/C@P-18-5/6D	/	5	32.8	9.2	3	/

Table S2. The surface elemental contents of CF, C@P-7 and C@P-18 obtained through XPS tests.

Samples	Elements content (%)							
	C	**O**	**N**	**P**	**S**	**O/C**	**P/S**	**P/N**
CF	86.99	12.33	0.68	/	/	0.14	/	
C@P-7-5	78.13	17.23	1.80	1.57	1.28	0.22	1.23	0.87
C@P-18-5	74.64	18.42	2.63	2.29	2.02	0.25	1.13	0.87

Table S3. TGA results of EP and its composites measured under nitrogen atmosphere.

	CF	**OCF**	**PZS**	**C@P-7-5**	**C@P-11-5**	**C@P-18-5**	**C@P-23-5**
Residual mass (wt%)	98.8	92.3	54.6	77.8	75.6	74.1	65.5

Table S4. Dynamic contact angles and surface energies of fibers.

Samples	Contact angle (°)		Surface energy (mN/m)		
	H_2O	CH_2I_2	γ_f^p	γ_f^d	γ_f
CF	71.6±1.1	68.0±2.1	12.3±0.1	24.0±0.2	36.2
C@P-7-5	66.3±0.6	63.0±1.0	14.1±0.2	26.8±0.2	40.9
C@P-11-5	64.0±1.1	62.6±1.5	15.4±0.1	27.1±0.1	42.5
C@P-18-5	62.2±0.6	60.6±0.6	16.0±0.2	28.2±0.1	44.2
C@P-23-5	60.6±2.0	60.2±2.3	16.9±0.1	28.5±0.1	45.4

Table S5. TGA results of EP and its composites measured under nitrogen atmosphere. [a]

Samples	$T_{5\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	φ_c (wt%)

EP	357.0	381.1	370.1	13.0
E/C	346.0	376.0	360.9	22.9
E/C/3D	331.4	368.2	345.7	23.3
E/C/6D	315.7	356.1	337.7	23.5
E/C/P/6D	297.0	357.0	342.2	24.8
E/C@P-18-5	297.7	344.9	328.8	24.6
E/C@P-18-5/3D	293.3	349.3	331.6	24.7
E/C@P-18-5/6D	288.3	356.0	338.4	25.1

a. $T_{5\%}$ and $T_{50\%}$: Temperatures at weight loss of 5 and 50 wt%, respectively.

T_{max}: Temperature at maximum degradation rate.

Table S6. The $E^{'}$ and T_g of epoxy and its composites.

	EP	**E/C**	**E/C/3D**	**E/C/6D**	**E/C/P/6D**	**E/C@P-18-5**	**E/C@P-18-5/3D**	**E/C@P-18-5/6D**
T_g **(℃)**	156.0	156.9	148.0	145.2	143.1	160.0	151.2	149.1
$E^{'}$ **(MPa)**	1749.1	1614.4	1852.6	3755.9	3731.1	3455.2	3622.9	4083.9

Table S7. The CCT testing results of representative samples.

Samples	**TTI (s)**	**PHRR (kW/m^2)**	**THR (MJ/m^2)**	**CO_2P (g/s)**	**COP (g/s)**	**EHC (MJ/kg)**	**TSP (m^2)**	**CY (wt%)**
E/C	88	740.4	71.2	0.42	0.22	25.1	17.4	20.7
E/C/6D	72	462.1	49.8	0.26	0.030	22.9	15.3	23.8
E/C/P/6D	69	523.1	55.0	0.28	0.030	22.3	14.8	23.6
E/C@P-18-5	68	685.7	59.8	0.40	0.028	24.6	13.4	23.4
E/C@P-18-5/6D	62	362.0	45.4	0.22	0.026	19.1	11.6	27.6

Table S8. The tensile modulus, tensile strength, elongation at break, flexural strength and impact strength of epoxy and its composites.

Samples	**Tensile modulus (MPa)**	**Tensile strength (MPa)**	**Elongation at break (%)**	**Flexural strength (MPa)**	**Impact strength (kJ/m^2)**
EP	1151.9±28.5	51.2±0.9	7.7±0.4	231.7±5.9	20.4±0.4
E/C	1086.1±16.2	51.8±0.8	4.7±0.2	196.1±15.7	19.6±0.5
E/C/3D	2228.8±30.7	54.4±1.8	3.3±0.1	\	17.7±2.5
E/C/6D	2715.8±70.8	63.1±1.1	2.8±0.2	216.3±6.1	15.9±1.9
E/C/P/6D	2683.3±40.4	58.7±2.1	2.7±0.1	\	15.1±0.5
E/C@P-7-5	1740.8±90.1	60.3±2.5	5.0±0.1	\	21.8±0.8
E/C@P-11-5	1837.6±48.1	63.6±0.5	5.2±0.1	\	22.6±0.5
E/C@P-18-5	1902.4±27.1	68.6±2.4	5.3±0.2	255.6±3.8	24.5±2.7
E/C@P-23-5	1850.0±62.4	64.3±2.0	4.8±0.1	\	23.5±0.5
E/C@P-18-5/3D	2350.1±52.1	69.8±2	4.5±0.1	\	20.4±1.4
E/C@P-18-5/6D	2811.9±44.2	72.9±3.4	4.4±0.2	294.0±7.1	19.6±0.3

Table S9. Comparison of tensile strength between the first measurement and the 30th measurement of representative specimens. The residual strain was also provided.

	EP	**E/C**	**E/C/6D**	**E/C@P-18-5**	**E/C@P-18-**

					5/6D
Tensile strength (MPa)	19.1±0.2	18.5±0.1	31.1±0.2	29.3±0.2	34.0±0.1
Tensile strength^{30} (MPa)^{a}	18.9±0.1	17.6±0.1	29.3±0.1	28.2±0.1	32.5±0.3
Residual strain (%)^{b}	0.16±0.01	0.19±0.01	0.28±0.01	0.15±0.01	0.2±0.01

a Tensile strength^{30} (MPa): Maximum stress of the composite specimen at the 30th cyclic tensile test.

b Residual strain (%): The strain of the composite specimen when the stress was zero after 30 cycles of tensile testing.

Table S10. Comparison of flame retardancy and mechanical properties of short carbon fiber-reinforced resin composites[49-53].

Mtrix	Fiber content	Methods of fiber modification	Flame retardant	Flame retardancy			Mechanicl properties	
				LOI	UL-94	CCT	Tensile strength	Elongation at break
EP(This work)	10%	In-situ grown PZS particles	6wt% of DOPO	51.7	V-0	PHRR:-51.1% THR: -36.3%	+40.7%	-6.4%
EP[49]	1%	Grafting silane coupling agents	/	/	/	PHRR:-13.5% TSP:-26.4%	+5.2%	/
EP[50]	1%	In-situ grown iron particles	4wt% of ammonium polyphosphate (APP)	27.5%	NR	THR:-22.5% TSP:-30.4%	-6.1%	-21.4%
EP[51]	1%	In-situ growth of metal-organic framework	4wt% of APP	28.9%	V-0	THR:-16.6% TSP:-27.3%	+8.1%	-14.3%
Poly(lactic acid) (PLA)[52]	15%	/	20wt% of aluminum hydroxide (ATH) and 5wt% aluminum hydroxide (MMT)	32%	V-0	PHRR:-57.9%	+16.8%	-33.2%
Thermoplastic polyurethane (TPU)[53]	20%	/	20wt% of silicon wrapped ammonium polyphosphate (SiAPP)	/	/	PHRR:-72.5% THR: -48.2%	/	/

● Supplementary Figures

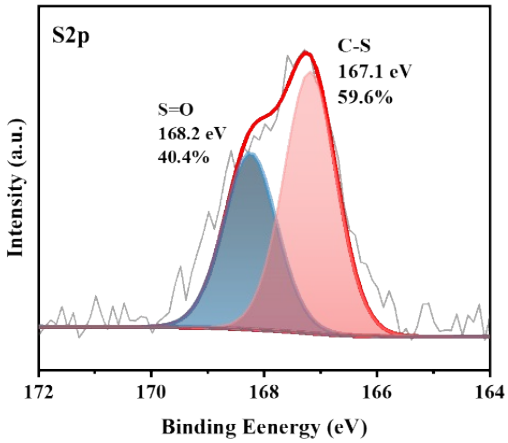

Figure S1. XPS S 2p spectrum of C@P-18-5 sample.

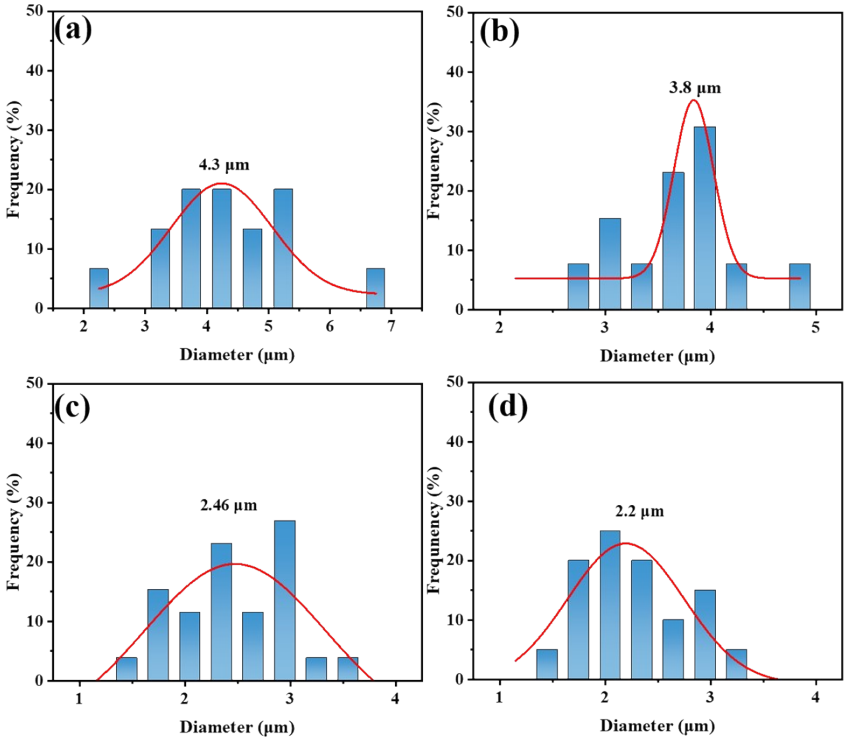

Figure S3. Diameter distribution of PZS particles on C@P fibers. The average diameters are also denotated. (a) C@P-7-5, (b) C@P-11-5, (c) C@P-18-5 and (d) C@P-23-5.

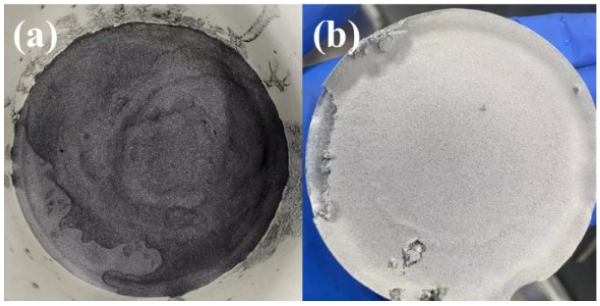

Figure S3. Digital photos showing the filter membrane appearance after vacuum-assisted filtrating (a) C@P-18 and (b) C@P-23. The sample was prepared at a reaction time of 5 h, and the ratio of two additions of HCCP was set at 1.5:1.

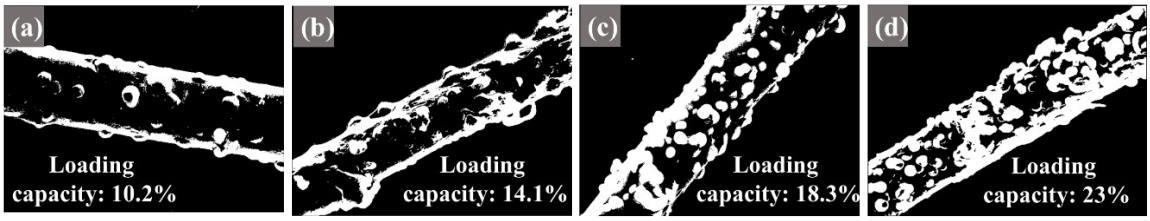

Figure S4. ImageJ-processed images display the surface particle loading of (a) C@P-7-5, (b) C@P-11-5, (c) C@P-18-5, and (d) C@P-23-5.

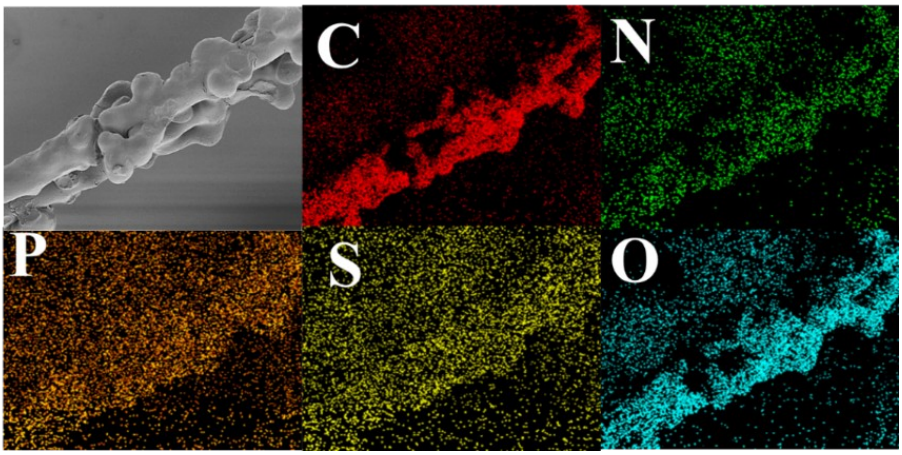

Figure S5. The EDS elemental mapping images of PZS nanoparticles on C@P-18-5 (where C represents carbon, N represents nitrogen, O represents oxygen, P represents phosphorus, and S represents sulfur). The sample was prepared at a reaction time of 5 h, and the ratio of two additions of HCCP was set at 1.5:1.

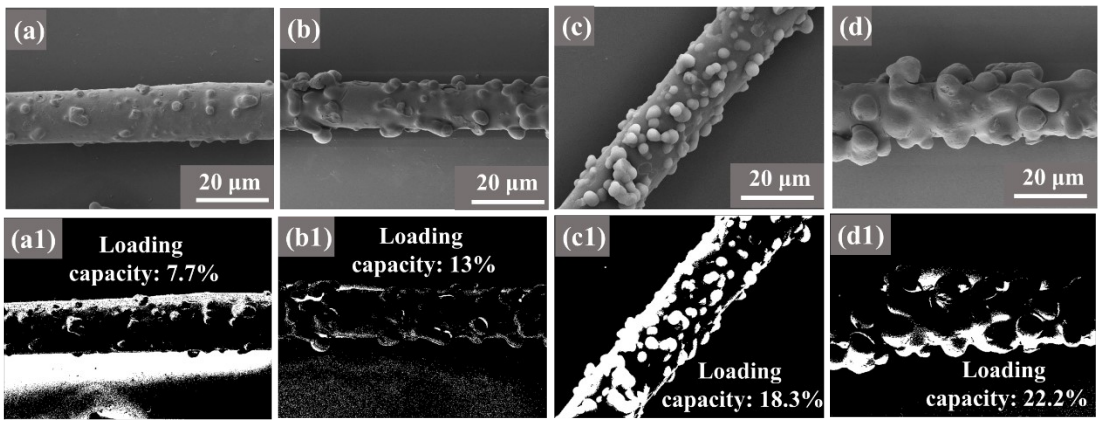

Figure S6. SEM images showing the morphologies of C@P-18 reacted for (a) 3 h, (b) 4 h, (c) 5 h, and (d) 6 h. ImageJ-processed images display the surface particle loading of C@P-18 for (a1) 3 h, (b1) 4 h, (c1) 5 h, and (d1) 6 h. The ratio of HCCP addition was 1.5:1.

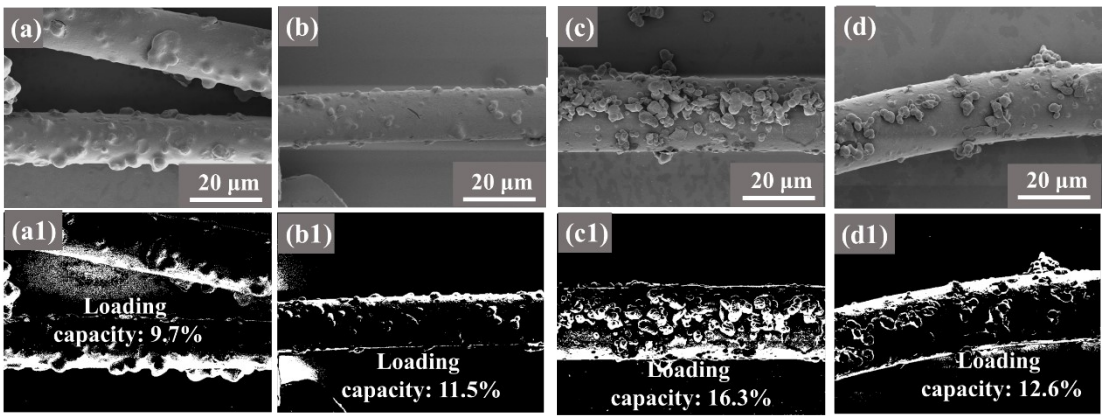

Figure S7. SEM images showing the morphologies of C@P-18-5 with the ratio of two additions of HCCP of (a) 2:1, (b) 1:1, (c) 1:1.5 and (d) 2:1. ImageJ-processed images display the surface particle loading of C@P-18-5 with the ratio of two additions of HCCP of (a1) 2:1, (b1) 1:1, (c1) 1:1.5 and (d1) 2:1. The reaction time was set at 5 h.

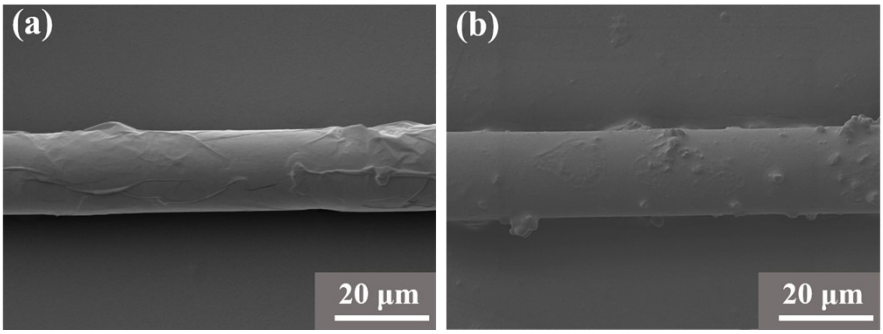

Figure S8. SEM images showing the morphologies of (a)C@H and (b) C@HB.

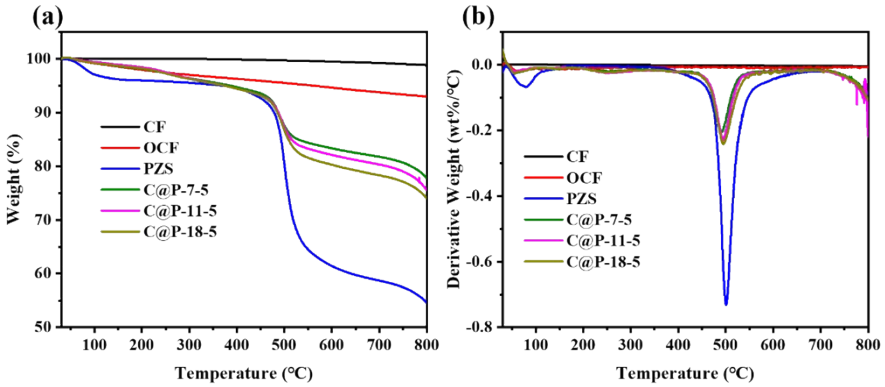

Figure S9. TGA (a) and DTG (b) curves of PZS, untreated CF, OCF and C@P samples.

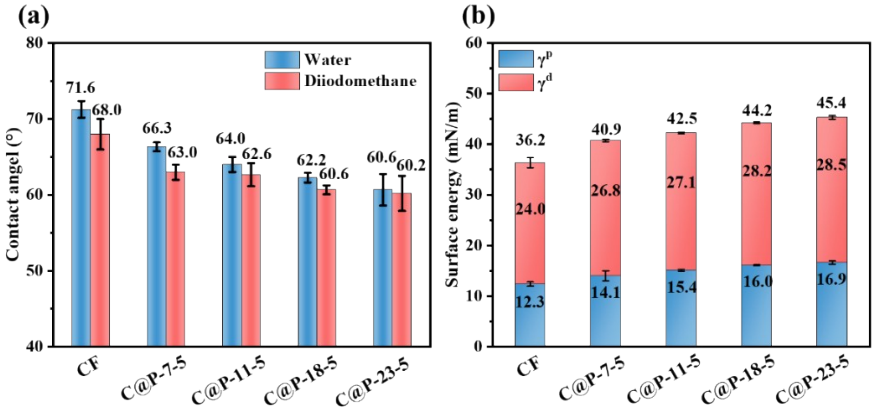

Figure S10. (a) Contact angles and (b) surface energies of untreated CF and the modified fibers as indicated.

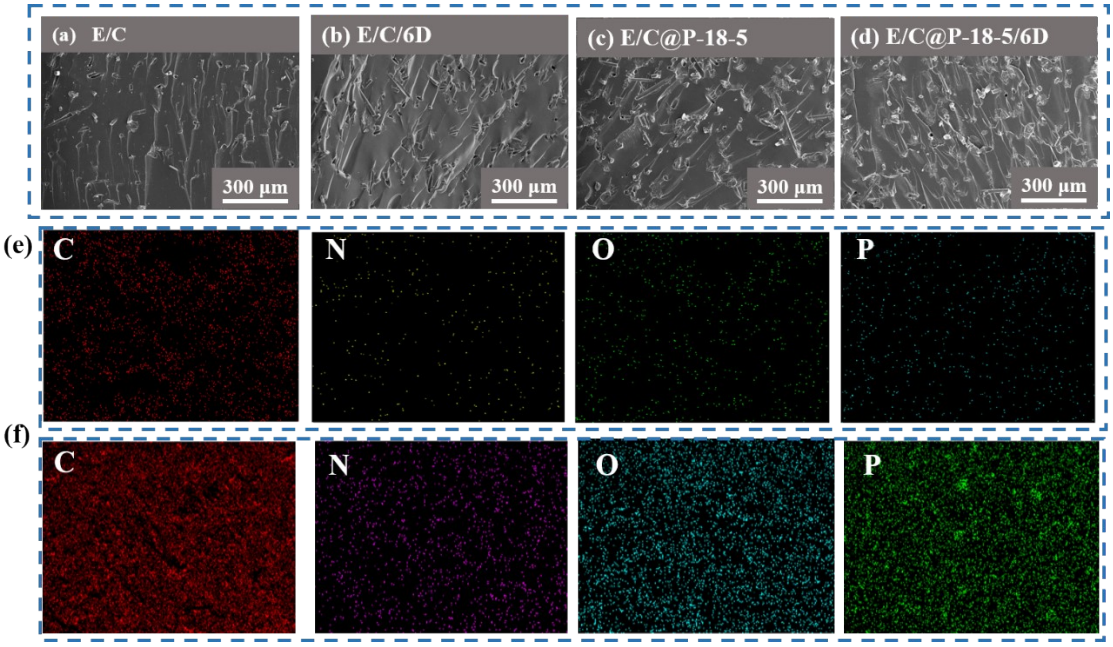

Figure S11. SEM images showing the fiber dispersion in the composites of (a) E/C, (b) E/C/6D, (c) E/C@P-18-5 and (d) E/C@P-18-5/6D. (e) and (f) showing the EDS elemental mapping images of DOPO in the (e) E/C/6D and (f) E/C@P-18-5/6D sample (where C represents carbon, N represents nitrogen, O represents oxygen and P represents phosphorus).

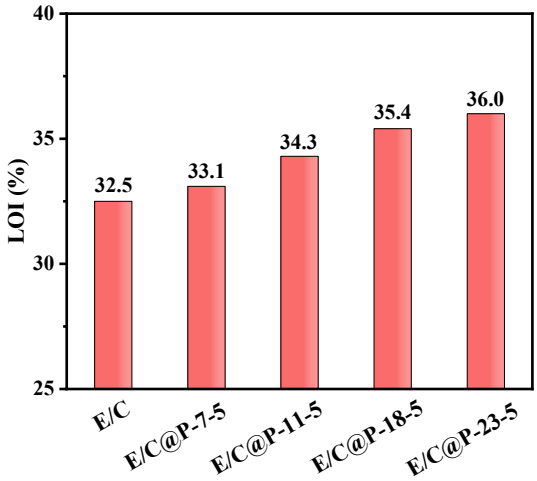

Figure S12. Comparison of LOI values among E/C@P-7-5, E/C@P-11-5and E/C@P-23-5 samples.

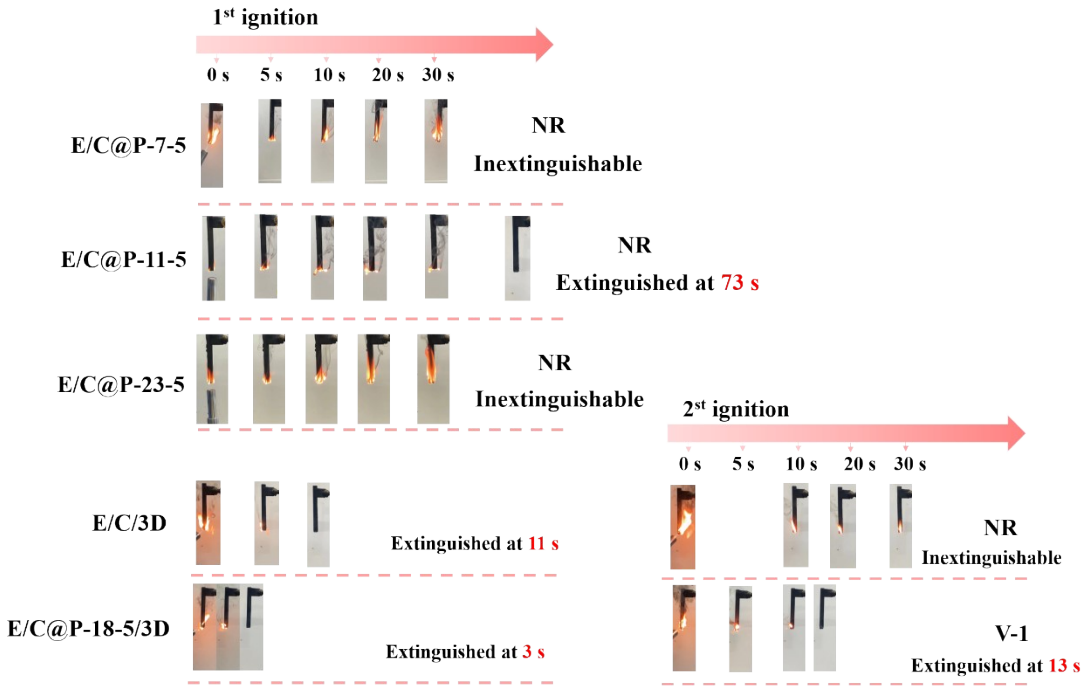

Figure S13. Digital photos showing the combustion behaviors of some samples as indicated in UL-94 testing.

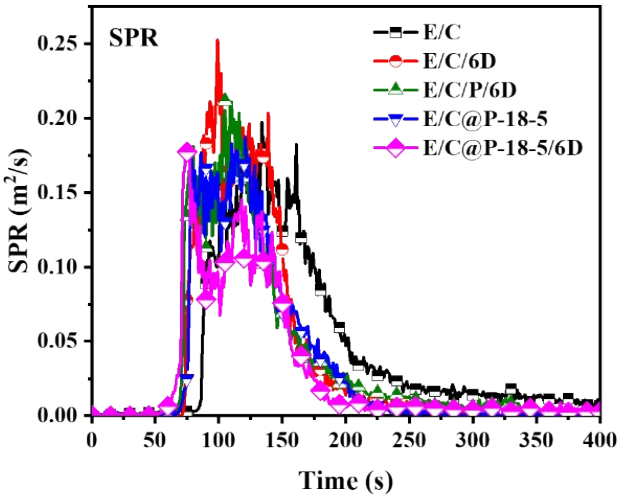

Figure S14. SPR curves of different samples obtained during cone calorimeter tests.

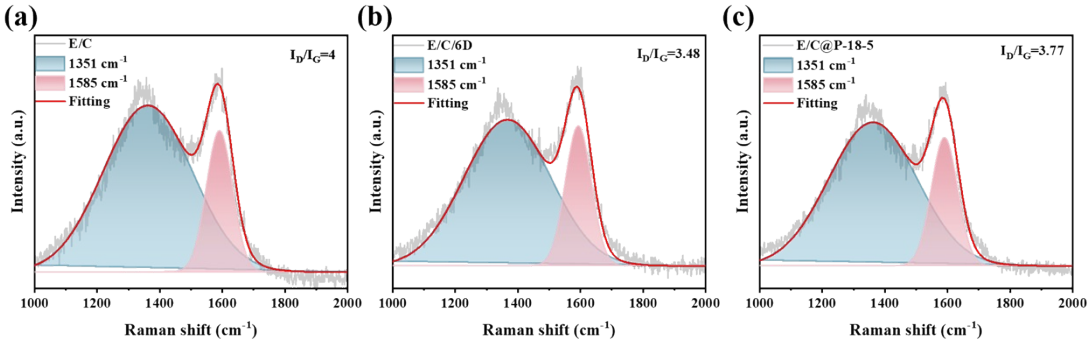

Figure S15. Raman spectra of the char residues of (a) E/C, (b) E/C/6D, and (c) E/C@P-18 samples after combustion.

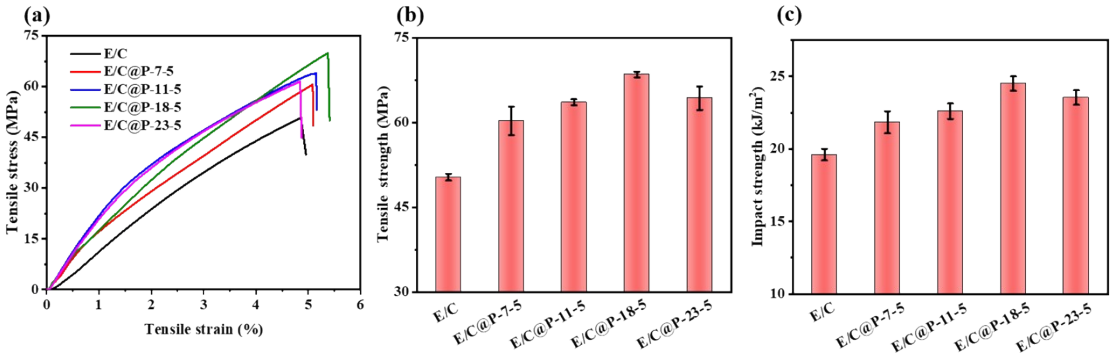

Figure S16. Mechanical properties of the representative composite samples as indicated in the graphs. (a) Stress-strain curves, (b) tensile strength, (c) unnotched Izod impact strength.

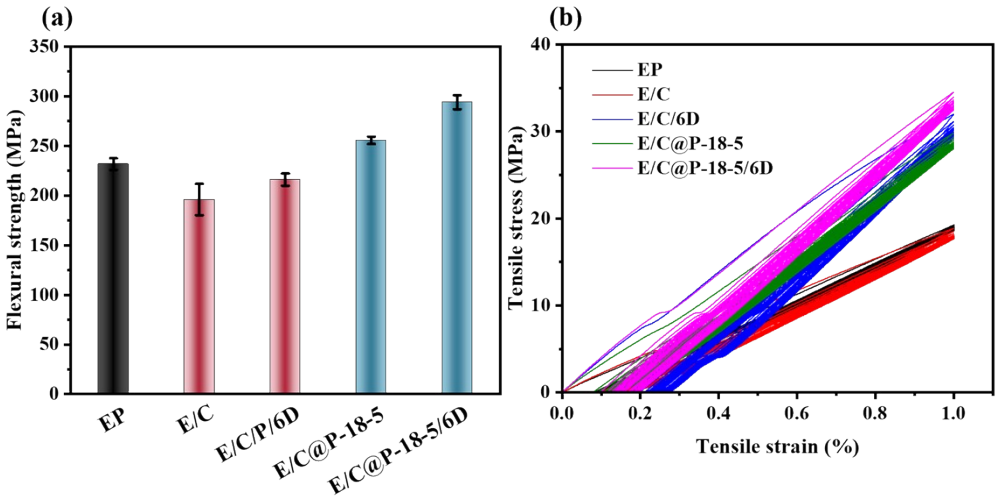

Figure S17. Mechanical properties of the representative composite samples as indicated in the graphs. (a) Flexural strength and (b) stress-strain curves of cyclic tensile testing.