Supporting Information

In situ interfacial assembly of P-MXene@COF hybrids for flame-retardant and smoke-suppressive epoxy resin

Yingbing Zou[a], Xinyuan Zheng[b], Xueyan Yang[b], Huixian Ye[a, *], Cheng Liu[a], Wentong Chen[a], Hongzhou Li[b, *]

[a] *Key Laboratory of Jiangxi Province for Special Optoelectronic Artificial Crystal Materials, Humic Acid Utilization Engineering Research Center of Jiangxi Province, College of Chemistry and Chemical Engineering, Jinggangshan University, Ji'an, 343009, China*

[b] *Engineering Research Center of Polymer Green Recycling of Ministry of Education, College of Environment and Resource Science, Fujian Normal University, Fuzhou, 350007, China*

Corresponding authors E-mail addresses: yehuixian@jgsu.edu.cn (H. Ye), lihongzhou@fjnu.edu.cn (H. Li)

Experimental section

Materials

Epoxy resin (EP, E-51) was obtained from Guangdong Kuibang Chemical Co., Ltd. (Guangdong, China). 4,4'-Diaminodiphenylmethane (DDM, 99%) and Acetic acid (99.7%) were obtained from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Titanium Aluminum Carbide (99.5%), Lithium Fluoride (99.9%), Ethanol (99.9%), (3-Aminopropyl)triethoxysilane (APTES, 98%), 4-aminobenzonitrile (98%), Trifluoromethanesulfonic acid (99%) and Terephthalaldehyde (98%) , Pyrophosphoric Acid (95%) were all obtained from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). All reagents were purchased and used without further purification. Deionized water was obtained in-house in the laboratory.

Synthesis

Synthesis of MXene

In brief, 2 g of lithium fluoride (LiF) was dissolved in 40 mL of hydrochloric acid and stirred for 5 min. Subsequently, 2 g of titanium aluminum carbide (Ti_3AlC_2) powder was slowly added into the etching solution at 35 °C and stirred for 24 h. After the reaction, the suspension was centrifuged at 3500 rpm for 5 min, and the solid residue was repeatedly washed with deionized water until the pH reached approximately 6, yielding the precipitate. The 1 g precipitate was redispersed in H_2O (250 mL) solution and subjected to ultrasonic treatment in an ice bath for 2 h. The resulting dispersion was centrifuged at 3500 rpm for 10 min, after which the supernatant was collected and freeze-dried under vacuum to obtain the dried MXene.

Synthesis of N-MXene

1 g of the collected MXene was dispersed in 300 mL of an EtOH/H_2O mixture (1:4, v/v) and was sonicated under a nitrogen atmosphere for 1 h. Subsequently, 4 mL of APTES was slowly added to the MXene dispersion, and the mixture was stirred continuously under a nitrogen atmosphere for 3 h. The resulting precipitate was washed several times with ethanol and ultrapure water, and was then freeze-dried to obtain N-MXene.

Synthesis of MXene@COF

2,4,6-Tris(4-aminophenyl)-triazine was synthesized according to our previously reported method [1]. Firstly, 1 g of N-MXene was dispersed in 50 mL of DMAc solution and was stirred for 10 min. Then, 2.41 g (0.018 mol) of terephthalaldehyde together with 10 mL of acetic acid was added into the dispersion, and the mixture was stirred for an additional 30 min to allow complete reaction between terephthalaldehyde and N-MXene. Subsequently, 3.57 g (0.01 mol) of 2,4,6-tris(4-aminophenyl)-triazine and 50 mL of 1,2-dichlorobenzene were introduced into the mixture. The resulting mixture was allowed to stand for 2 h, after which the light green product was collected by vacuum drying.

Synthesis of P-MXene@COF

First, 5 g of pyrophosphoric acid was dissolved in 100 mL of deionized water. Then, 5 g of MXene@COF was slowly added to the solution at 0 °C, and the mixture was stirred under low temperature for 2 h. The resulting suspension was filtered, and the yellow-brown solid product was collected after vacuum drying.

Preparation of EP composites

EP composites were prepared by blending method. Firstly, P-MXene@COF was added

into EP after grinding and sieving (200 mesh) at a certain mass ratio (mass of flame retardant: total mass of composite), and then stirred at 100°C for 30 min. After the filler was homogeneously dispersed, DDM curing agent was added, and then stirred for 5 min to homogeneously dispersed the DDM curing agent. After vacuum treatment for 3 min, the mixture was poured into preheated PTFE molds. Subsequently, the curing was carried out in stages at 100°C for 30 min, 120°C for 2 h and 150°C for 2 h. The curing time was then adjusted to the temperature of the molds. The detailed ratios of the components are listed in Table S1.

Measurement

Thermal gravimetric analysis (TGA) was carried out by using a TG209F3 thermogravimetric analyzer (NETZSCH, Germany) with a linear heating rate of 10 °C/min (30 °C to 800 °C). Differential scanning calorimetry (DSC) was carried out on a setline DSC (Waters Q20, UK) instrument at a heating rate of 10 °C/min under a N_2 atmosphere. Fourier transform infrared spectroscopy (FTIR) was performed by using an FTIR spectroscope (Thermo Fisher's NICOLET IS10, USA) following the KBr disc method. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed using a Hitachi Regulus 8100 instrument and an EDAX Octane Elect Plus instrument. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) testing was performed using an Agilent 5800 instrument, with each sample analyzed three times and the results averaged. X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB Xi^+ (Thermo Fisher Scientific). Raman spectroscopy was performed by using a Via Qontor Raman spectrometer (Thermo Fisher DXR2xi, USA) with a laser light source at 532 nm. Thermogravimetric analysis/infrared spectrometry (TG-IR) was performed by using a TGA4000+SP2 (Thermo Fisher Scientific) TG-IR instrument at a heating rate of 10 °C/min from 30 °C to 800 °C in a N_2 atmosphere. According to the ISO-5660 standard

procedures, 100 × 100 × 3 mm^3 specimens, each with a weight of approximately 35 ± 0.2g, were prepared for cone calorimeter testing (iCone Classic, Fire Testing Technology, UK) at a 35 kW/m^2 heat flux. The limiting oxygen index (LOI) was evaluated based on ASTM D2863 by a JF-3 oxygen index meter (Hesheng Analysis Instrument Co., Ltd., China). The size of the sample was 130 × 6.5 × 3 mm^3. UL-94 vertical burning tests were carried out on an RSJ-5 horizontal-vertical burning tester (Hesheng Analysis Instrument Co., Ltd., China) according to ASTM D3801, using specimens with dimensions of 130 × 6.5 × 3 mm^3. The mechanical properties were examined with the dynamic mechanical analysis (DMA, Netzsch 242E, 1Hz, 40-250 °C, 2 °C min^{-1}) and 3-point bending test. Tensile strength of composites and remolded composites were tested using a universal testing machine (SANs, China). The impact strength was measured by cantilever beam impact tester (MTS SYSTEMS, Co., Ltd., China), with an unnotched sample with a size of 80 × 10 × 4 mm^3. For LOI, UL-94 and mechanical testing (tensile and impact), five specimens were measured for each formulation, and the reported values represent the average of these five measurements. Density functional theory (DFT) calculations were performed to optimize the geometries of the monomers and oligomers at the B3LYP/6-311G(d) level of theory. Molecular configuration optimization and electrostatic potential (ESP) mapping were conducted using the CP2K program. Interaction-region indicator (IRI) isosurfaces of the model systems were generated and analysed with the Multiwfn program, using geometries optimised with CP2K.

The fire performance index (FPI) is calculated as follows:

$$FPI = \frac{TTI}{pHRR}$$

where TTI is the time to ignition and pHRR is the peak heat release rate.

The fire growth index (FGI) is calculated as follows:

$$FGI = \frac{pHRR}{T_{pHRR}}$$

where T_{pHRR} is the time to pHRR.

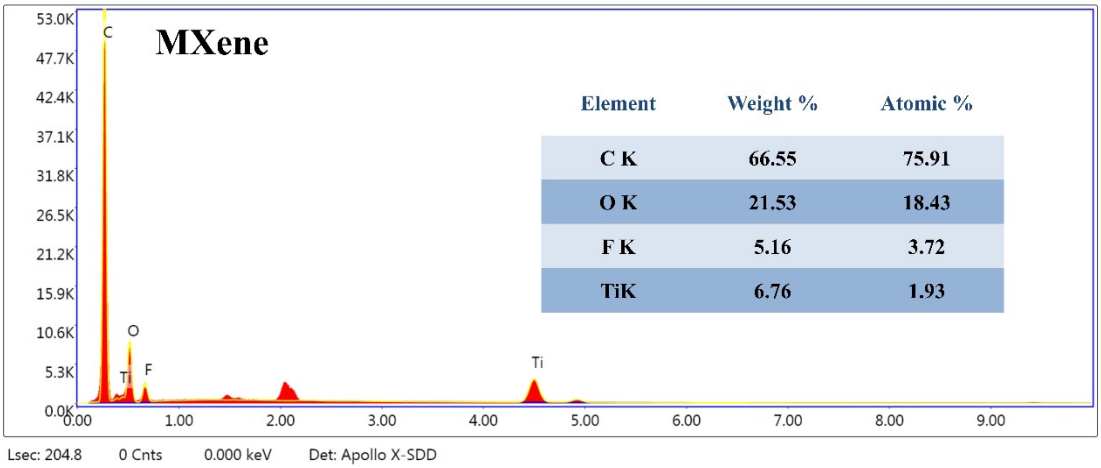


Figure S1. The EDS sum spectrum and elemental composition of MXene.

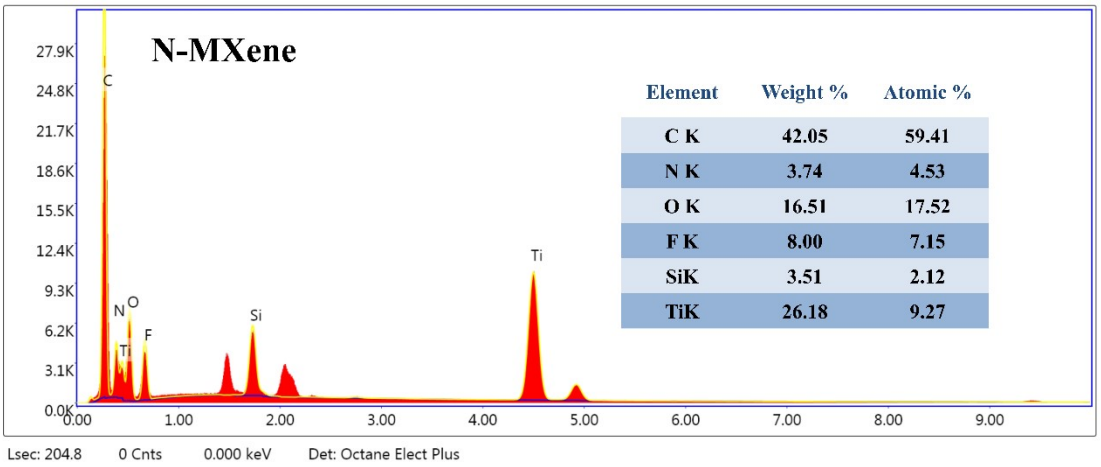


Figure S2. The EDS sum spectrum and elemental composition of N-MXene.

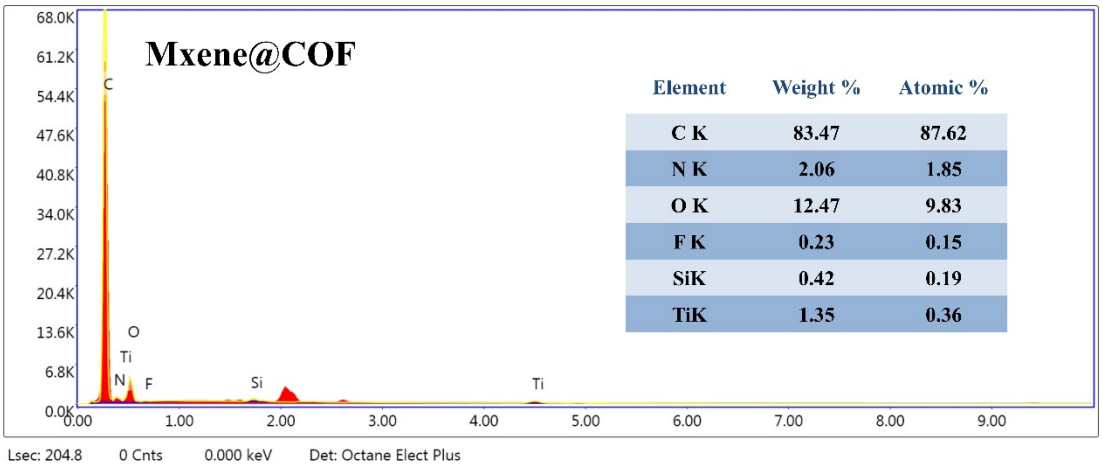
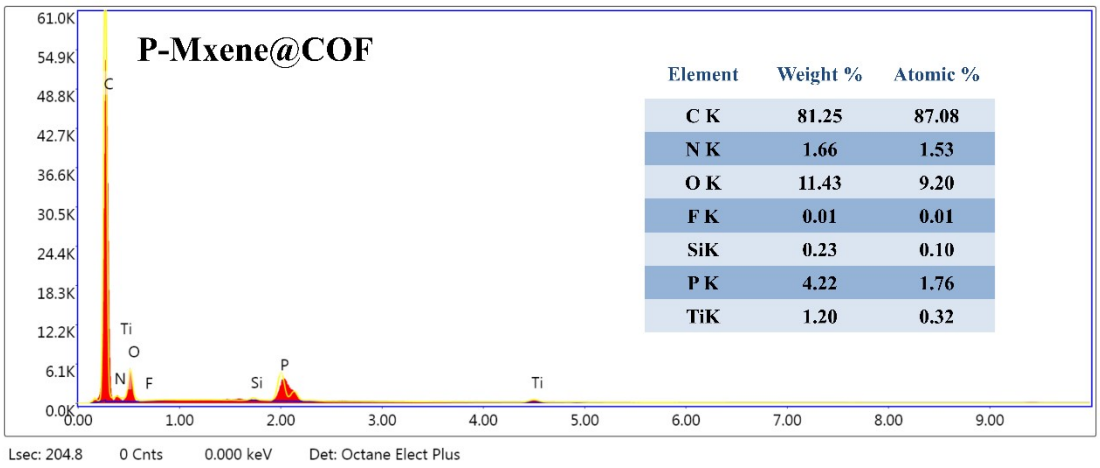


Figure S3. The EDS sum spectrum and elemental composition of MXene@COF.



Element	Weight %	Atomic %
C K	81.25	87.08
N K	1.66	1.53
O K	11.43	9.20
F K	0.01	0.01
SiK	0.23	0.10
P K	4.22	1.76
TiK	1.20	0.32

Figure S4. The EDS sum spectrum and elemental composition of P-MXene@COF.

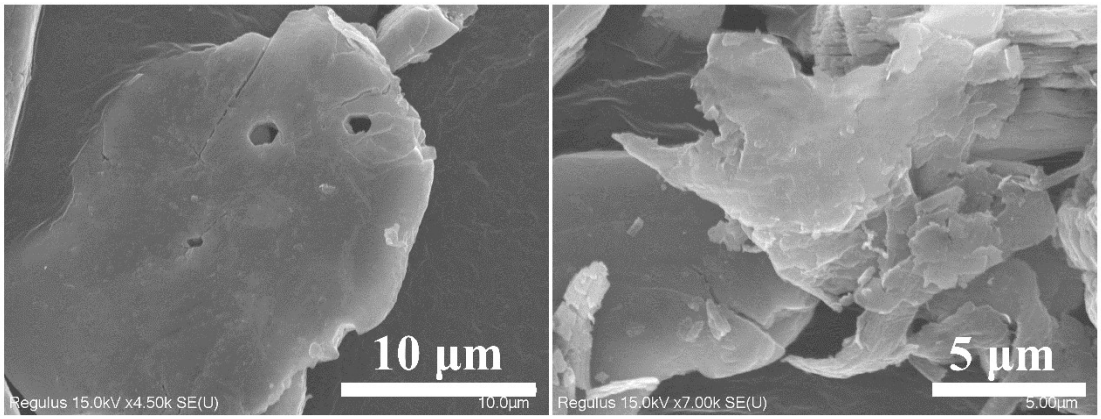


Figure S5. The SEM images of N-MXene.

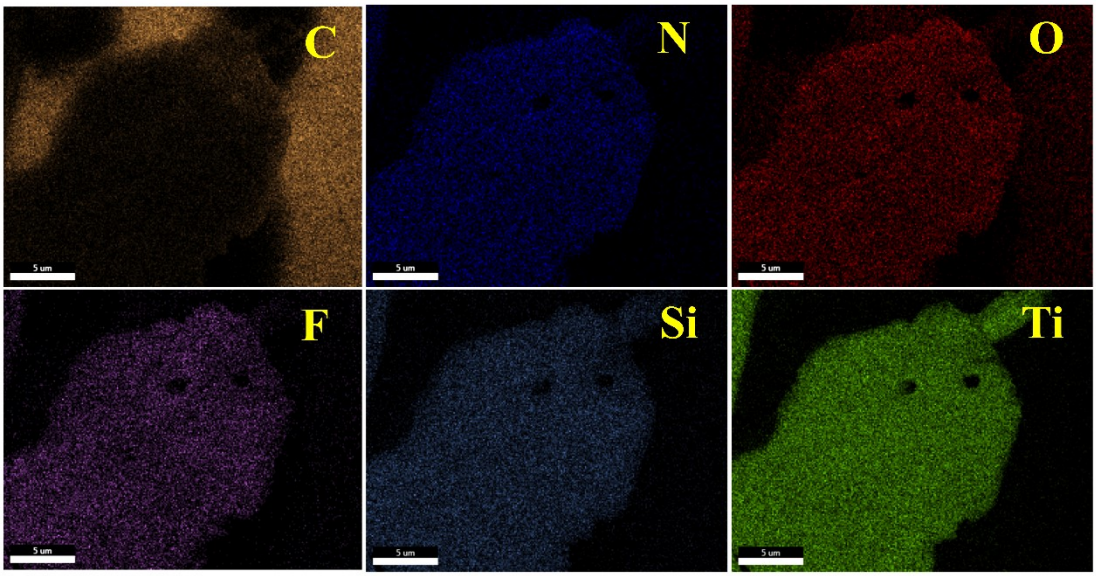


Figure S6. The EDS mappings of N-MXene.

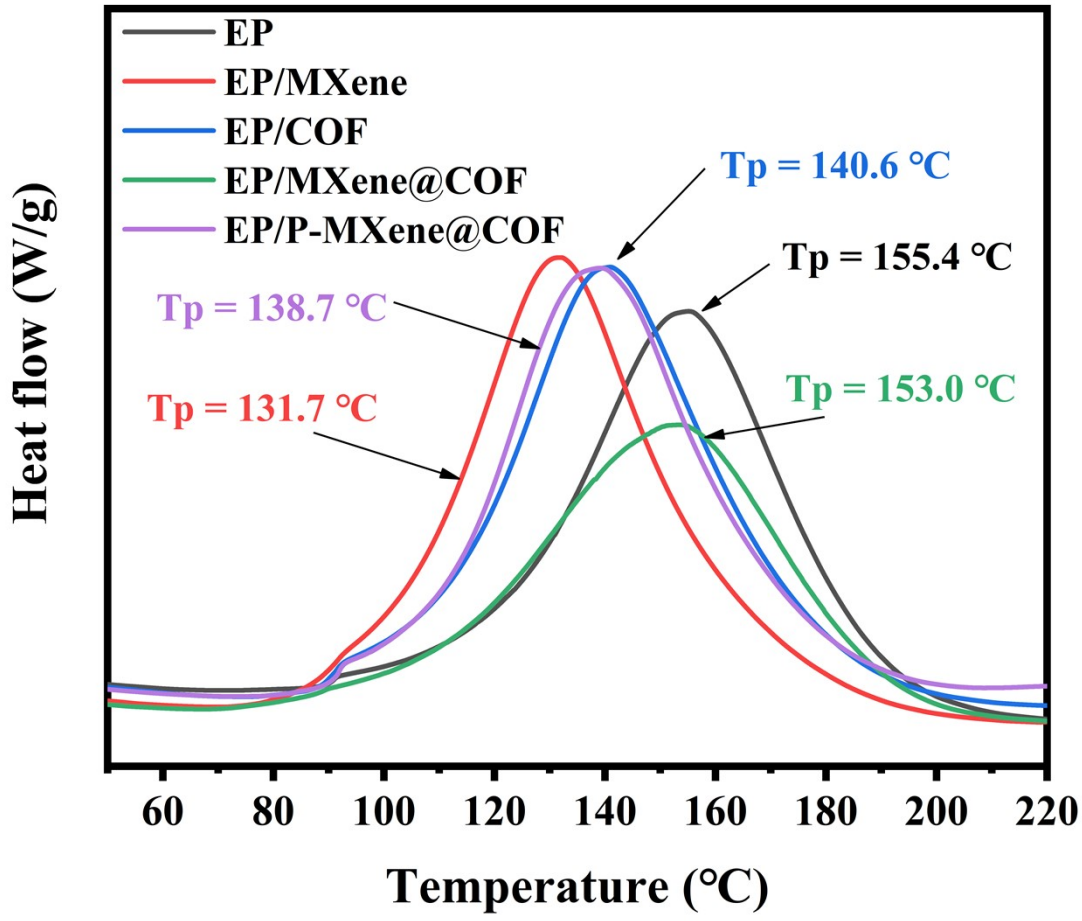


Figure S7. DSC curves of EP and EP composites.

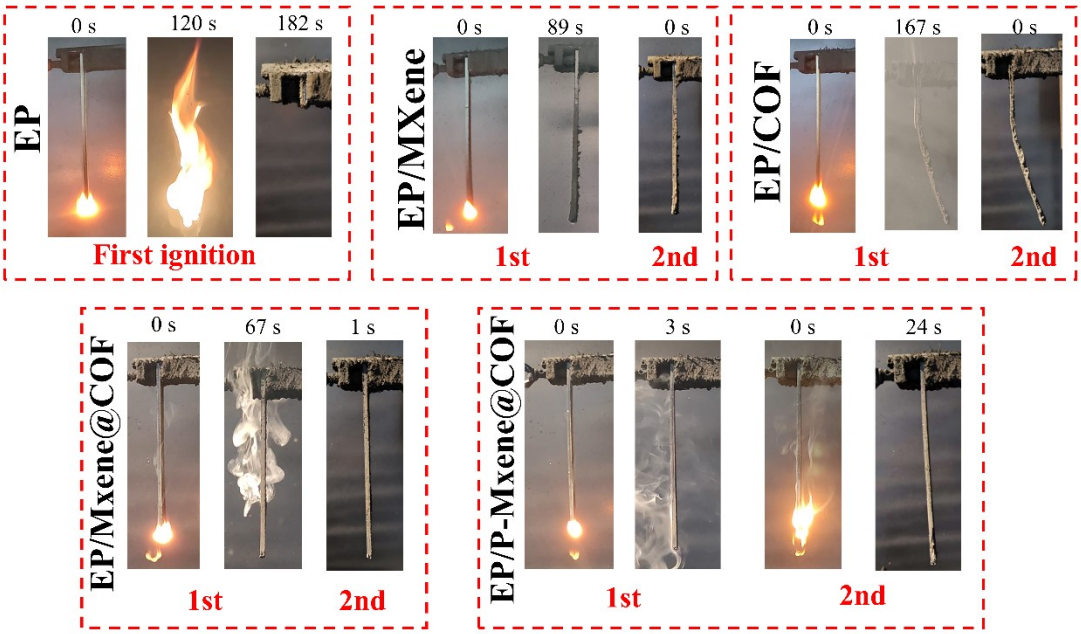


Figure S8. The UL-94 vertical burning of EP and EP composites.

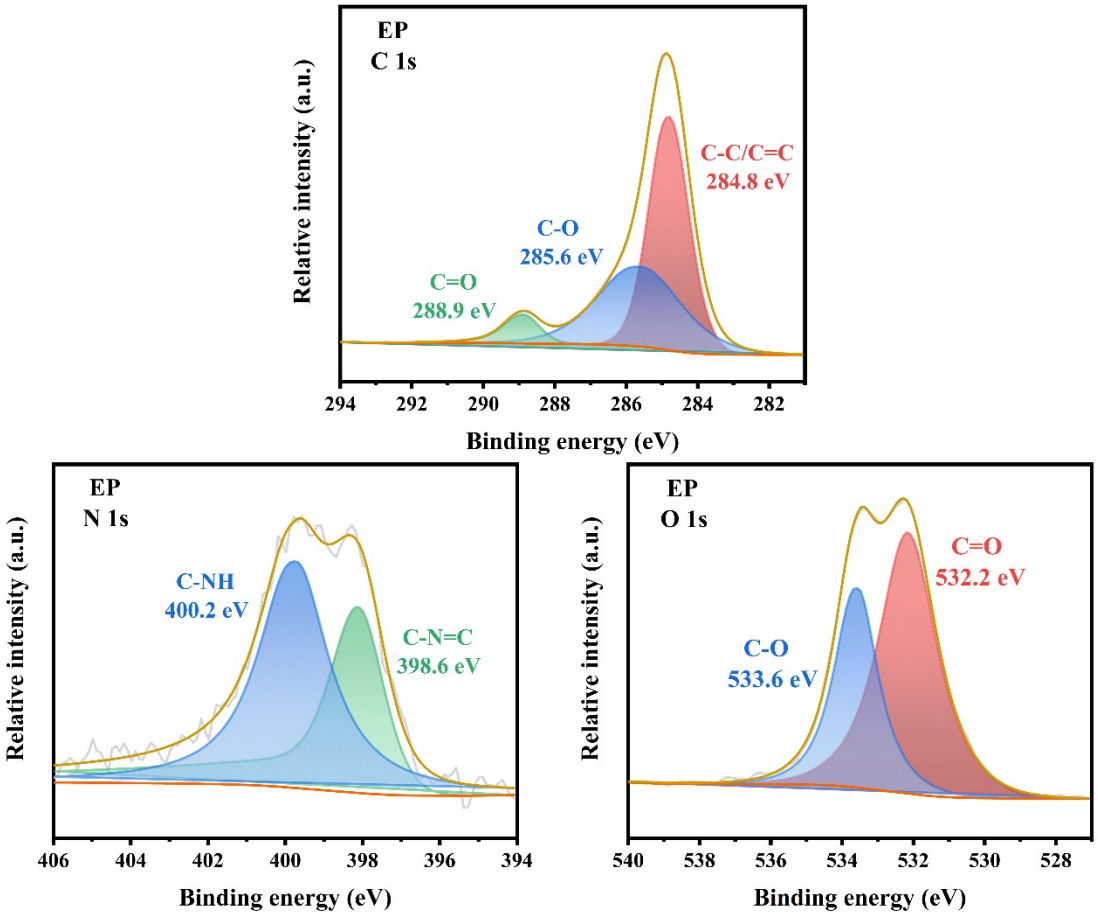


Figure S9. C 1s, O 1s and N 1s XPS spectra of the char residues

Table S1. ICP-OES test results for P-MXene@COF.

Number	1	2	3
Mass (g)	0.0461	0.0461	0.0461
Constant volume (mL)	20	20	20
Element tested	P	P	P
Element concentration in test solution (mg/L)	9.0336	8.5984	8.7404
Dilution factor	10	10	10
Element concentration in digested/original solution (mg/L)	90.3360	85.9837	87.4036
Element content in sample (mg/kg)	39191.32	37303.12	37919.13
Element content in sample (wt%)	**3.9191**	**3.7303**	**3.7919**

Table S2. Formulae of EP and EP composites

Samples	EP (wt%)	FR (wt%)	DDM (wt%)	FR ratio (wt%)
EP	80	0	20	0
EP/MXene	77.5	3	19.5	3
EP/COF	77.5	3	19.5	3
EP/MXene@COF	77.5	3	19.5	3
EP/P-MXene@COF	77.5	3	19.5	3

Table S3. Critical data of TGA test

Atmosphere	Samples	Char residue at 800℃ (%)	$T_{5\%}$ (°C)	T_{max} (°C)	Maximum mass loss rate (%/min)
N_2	EP	16.7	370.4	387.4	19.2
	EP/MXene	16.4	372.4	387.9	20.1
	EP/COF	16.7	370.9	387.9	18.3
	EP/MXene@COF	17.8	367.2	386.2	18.5
	EP/P-MXene@COF	22.1	356.8	381.3	11.8
Air	EP	1.1	372.3	384.8	16.3
	EP/MXene	2.2	371.9	384.9	16.7
	EP/COF	1.6	361.5	382.5	14.1
	EP/MXene@COF	0.6	370.4	382.9	13.9
	EP/P-MXene@COF	0.7	355.4	379.4	10.4

Table S4. DMA datas of EP and EP composites

Samples	T_g (°C)	E' (MPa, 40 °C)	E' (MPa, Tg + 40 °C)	v_e (10^3 mol/m^3)
EP	161.1	2188.6	25.0	2.11
EP/MXene	157.9	1990.3	28.5	2.43
EP/COF	180.0	1760.3	28.4	2.31
EP/MXene@COF	153.6	2172.0	30.4	2.61
EP/P-MXene@COF	157.5	1826.6	27.4	2.33

Table S5. Mechanical properties of EP and EP composites.

Samples	Elongation at break (%)	Tensile strength (MPa)	Impact strength (kJ/m^2)
EP	7.3	51.3±5.8	8.3±0.3
EP/MXene	7.5	46.0±6.2	7.8±0.6
EP/COF	10.3	59.9±2.8	8.9±0.4
EP/MXene@COF	7.8	60.8±3.7	8.4±0.3
EP/P-MXene@COF	7.2	53.5±4.9	8.2±0.4

Table S6. Cone calorimetry data of EP and EP composites.

Samples	EP	EP/MXene	EP/COF	EP/MXene@ COF	EP/P-MXene@ COF
TTI (s)	82	70	98	82	70
pHRR (kW/m^2)	1022.6	795.1	892.2	784.8	578.1
THR (MJ/m^2)	81.5	71.8	87.0	74.1	63.5
pSPR (m^2/s)	0.31	0.29	0.26	0.27	0.24
TSR (m^2/ m^2)	3124.8	2700.6	3215.5	2997.6	2734.8
TSP (m^2)	27.6	23.9	28.4	26.5	24.2
pCOPR (g/s)	0.033	0.026	0.028	0.030	0.024
pCO_2PR (g/s)	0.58	0.43	0.52	0.43	0.32
pMLR (g/s)	0.40	0.37	0.38	0.40	0.28
Char yield (%)	10.0	7.5	6.9	14.3	19.4
FPI (m^{2}s/kW)	0.080	0.088	0.110	0.105	0.121
FGI (kW/m^2/s)	8.18	7.57	6.37	7.13	4.45
pEHC (MJ/kg)	24.2	21.5	22.4	21.9	20.5
COY (kg/kg)	0.100	0.080	0.074	0.079	0.090
CO_2Y (kg/kg)	1.54	1.32	1.38	1.30	1.29

Table S7. Fire behavior of flame retardants based on MXene and COFs.

Type of FRs	Loading (wt%)	pHRR reduction (%)	THR reduction (%)	Reference
DOPO@COF	3	39.0	18.7	1
H-MX	4	31.6	9.5	2
MXene@LDH	2	25.3	24.4	3
MXene@Bi-MOF	2	28.8	36.5	4
CoNi-ZIF/MXene	2	22.7	/	5
MXene-PCN	2	27.3	12.2	6
PA-COF@BN	4	31.6	39.4	7
DOPO-COFs	3.2	18.4	18.5	8
FCOF	3.2	19.7	/	9
APP@COF	2	54.7	7.4	10
P-MXene@COF	**3**	**43.4**	**22.2**	**This Work**

References

1 Y. Zou, Z. Shi, J. Shi, F. Luo and H. Li, *Constr. Build. Mater.*, 2024, **426**, 136166.

2 J. Wang, L. Li, K. Yu, Y. Jia, J. Zhang, Z. Wang, Y. K. K. Richard and Y. Lu, *Constr. Build. Mater.*, 2025, **464**, 140124.

3 K. Zhou, K. Gong, F. Gao and L. Yin, *Compos. Part A Appl. Sci. Manuf.*, 2022, **157**, 106912.

4 K. Gong, L. Cai, C. Shi, F. Gao, L. Yin, X. Qian and K. Zhou, *Compos. Part A Appl. Sci. Manuf.*, 2022, **161**, 107109.

5 X. Qian, C. Shi, M. Wan, H. Che and J. Li, *ACS Appl. Nano Mater.*, 2025, **8**, 2130-2140.

6 L. Ma, H. Ge, J. Gao and Z. Zhu, *Prog. Org. Coat.*, 2025, **207**, 109407.

7 J. Liu, Y. Zhang, Y. Yu and X. Ji, *New J. Chem.*, 2025, **49**, 18006-18017.

8 X. Mu, D. Wang, Y. Pan, W. Cai, L. Song and Y. Hu, *Compos. B. Eng.*, 2019, **164**, 390-399.

9 X. Mu, J. Zhan, C. Ma, Y. Pan, F. Chu, L. Song and Y. Hu, *Compos. Part A Appl. Sci. Manuf.*, 2019, **117**, 23-33.

10 X. Bi, H. Di, J. Liu, Y. Meng, Y. Song, W. Meng, H. Qu, L. Fang, P. Song and J. Xu, *Adv. Compos. Hybrid Mater.*, 2022, **5**, 1743-1755.