Supporting Information

Nano SiC ceramics and MOFs Synergistic Enhanced Polylactic Acid Composites for Efficient Flame Retardant Performance

Feng Wei[a], Ding Chen[a,b]*, Can Wei[a], Hao Huang[a], Haixiang Tang[a], Yu Chen[e]*, Nannan Wang[a]*, Chunze Yan[d], Yanqiu Zhu[a,c]

[a] State Key Laboratory of Featured Metal Materials and Life-cycle Safety for Composite Structures, MOE Key Laboratory of N ew Processing Technology for Nonferrous Metals and Materials, School of Resources, Environment and Materials, Guangxi University, Nanning 530004, China.

[b] School of Electronic Engineering, Guangxi Engineering Research Center for Characteristic Metallic Powder Materials, Guangxi University of Science and Technology, Liuzhou 545006, China.

[c] Faculty of Environment, Science and Economy, University of Exeter, EX4 4QF, United Kingdom.

[d] State Key Laboratory of Materials Processing and Die & Mould Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, People's Republic of China

[e] Department of Materials, Design and Manufacturing Engineering, School of Engineering, Harrison Hughes Building, University of Liverpool, Liverpool, L69 3GH, U.K.

Corresponding author. E-mail address: wangnannan@gxu.edu.cn （Nannan Wang）

Characterization

X-ray diffraction (Rigaku D/MAX 2500V, Japan) was used to evaluate the crystal structure analysis with a step size of 0.02° in the 2θ range of 5-80°. Fourier transform infrared (FTIR) spectroscopy performed on an FTIR400 spectrometer (PerkinElmer Instrument, US) studied the chemical structure of the samples. FTIR spectra were obtained in the wavenumber range of 4000-400 cm^{-1} with a 4 cm^{-1} over 16 scans. The mechanical properties of the composites were tested by the Mechanics of Materials Experiment System (Model Spec 8801, INSTRON, UK) at a 10mm/min rate at room temperature. At least four samples of each material were tested and averaged. The surface morphology of the phase morphology of Reinforced phase filler was observed using a scanning electron microscope (SEM, Sigma 300, ZEISS, Germany) operating at 5 kV and a thin layer of gold was pre-painted on the samples. Energy Disperse Spectroscopy (EDS, Sigma 300, ZEISS, Germany) was used to obtain the EDS mapping of Si and Cu to investigate particles' particle distribution. Thermogravimetric analysis of particles (TGA, Perkin Elmer-4000, USA) was performed in a dry nitrogen atmosphere at a scan rate of 10℃/min over a temperature range of 30-800℃. The PLA and its composites' melting and crystallization temperature profiles were obtained by dynamic differential scanning. Differential scanning calorimetry was performed with a Mettler instrument calibrated with indium (T, ΔH) and zinc (T). The samples were heated in DSC from 30℃ to 200℃ with a heating rate of 10℃·min^{-1} and then cooled from 200℃ to 30℃ with a rate of 10℃·min^{-1}, loop twice to get the second test data. Two repeats of each sample were carried out. A combustion test was performed on a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660 standard procedures, with 3mm×100cm^2 specimens. Each specimen was exposed

horizontally to 35kW/m^2 external heat flux. All samples were tested two times. Laser Raman spectroscopy (LRS) measurements were carried out with a SPEX-1403 laser Raman spectrometer (SPEX Co., United States) at room temperature with excitation provided in backscattering geometry by a 532nm argon laser line. Thermogravimetric analysis–infrared spectrometry (TG–IR) was performed using a TGA4000 thermogravimetric analyzer connected to an IR400 FTIR spectrophotometer (Perkin Elmer, USA). The samples were put in an alumina crucible and heated from 30 to 800℃. The heating rate was 20℃/min (nitrogen atmosphere, flow rate of 40ml/min). To use a VG ESCALB MK-II Electron Spectrometer (Al K excitation source at 1486.6 eV), X-ray photoelectron spectroscopy (XPS) was conducted on the samples to confirm the elemental composition of SiC_e, HK_p, and SiC_e/HK_p particles in the PLA composites chars and hybrids. Pyrolysis-gas chromatography/mass spectrometry (PY-GC–MS) was performed on a TG-GC-MS system (Perkin Elmer, USA). The pure PLA and its composites were heated to 800℃ at a heating rate of 20℃/min. The data of mass spectra were examined by the NIST library.

Thermal properties characterization of PLA and its composites

Table S1. TGA and DTG data of PLA and its composites under an N_2 atmosphere.

Samples	T_s (℃)	T_p (℃)	Residues at 700℃ (%)
PLA	287.9	471.3	3.9
P-S	283.8	474.0	5.3
P-H	293.1	476.6	4.7
P-S/H-0.5%	298.7	477.2	4.9
P-S/H-1%	298.7	477.9	5.1
P-S/H-2%	296.1	477.4	5.5
P-S/H-3%	297.5	478.0	5.8

P-S/H-4%	294.4	476.7	7.0

Table S2. Summary of DSC results of PLA and its composites.

Sample Name	$T_{m\text{-}onset}$ (℃)	$T_{c\text{-}onset}$(℃)	ΔH_m	χ_c/%
PLA	98.5	130.0	28.2	30.1
P-S	99.7	129.5	25.4	27.7
P-H	98.5	129.6	27.8	30.3
P-S/H-0.5%	99.8	130.2	24.7	26.5
P-S/H-1%	99.4	129.6	23.9	25.8
P-S/H-2%	97.9	129.8	26.8	29.2
P-S/H-3%	100.9	129.2	25.2	27.8
P-S/H-4%	99.1	129.2	25.8	28.7

χ_c was obtained from the ratio of the areas under the heat absorption peaks of the composite and pure PLA samples, Calculated by formula (1) below:

$$\chi_c = \frac{\Delta H_m}{(1 - \varphi)\Delta H_m^*} \times 100 \quad (1)$$

where φ is the weight fraction of the dispersed phase in the blend, ΔH_m is the actual enthalpy of melting calculated from the melting peak in the DSC curve (J/g), and ΔH_m^* is the enthalpy heat of pure PLA crystals; the enthalpy of melting for 100% crystalline PLA is 93.6J/g[1].

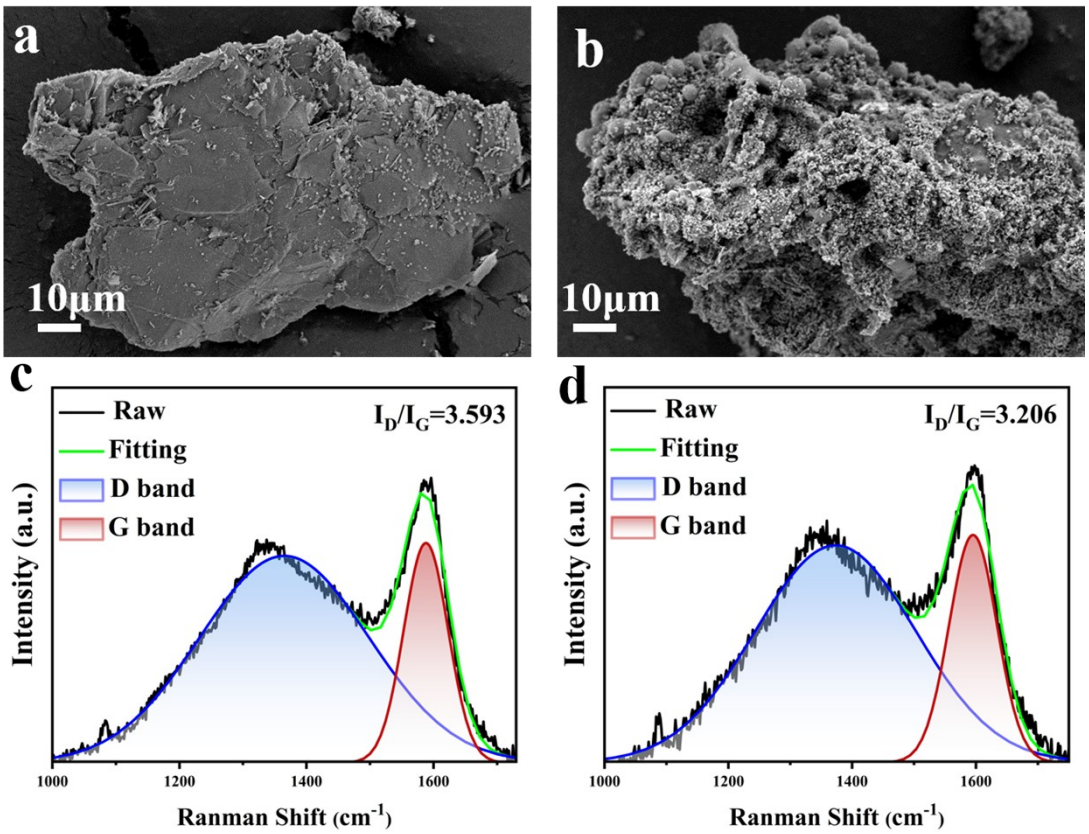
Forced flaming of PLA and its composites

74

75 Table S3 Fire test data of PLA and its composites

Sample	TTI	pHRR (kW/m^2)	THR (MJ/m^2)	pSPR (m^2/s)	TSR (m^2/m^2)	AEHC (MJ/KG)	FRI
PLA	18s	590.8	88.0	0.023	378.2	31.5	1.00
P-S	23s	393.9	58.6	0.024	274.5	23.8	2.88
P-H	25s	532.3	73.2	0.033	749.7	28.1	1.85
P-S/H-0.5%	19s	442.1	49.5	0.024	188.4	21.9	2.51
P-S/H-1%	23s	440.5	61.1	0.026	505.3	27.7	2.47
P-S/H-2%	18s	438.3	53.0	0.028	292.8	25.1	2.24
P-S/H-3%	22s	390.6	72.0	0.021	293.1	29.1	2.26
P-S/H-4%	23s	423.1	61.7	0.024	396.8	25.9	2.54

76



77

78 Fig.S1. SEM images of char residue: (a) P-H, (b) P-S; Raman profiles of char residue: (c) P-H, (d)

79 P-S.

Reference

[1] L. Liu, Y. Xu, Y. Di, M. Xu, Y. Pan, B. Li, Simultaneously enhancing the fire retardancy and crystallization rate of biodegradable polylactic acid with piperazine-1, 4-diylbis (diphenylphosphine oxide), Composites Part B: Engineering 202 (2020) 108407.