Supporting Information

Synthesis of a phosphorus-containing nickel(II) complex towards suppressing heat release and enhancing fire safety of polyamide 6

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1. Characterization

Nuclear magnetic resonance (NMR) measurements including the ^{1}H NMR of BPM and BPMNi, as well as ^{31}P NMR of DOPO, BPM and BPMNi were evaluated using an Avance 3HD 600 MHz NMR spectrometer (Bruker Co., Switzerland). DMSO-d_6 was chosen as the deuterated solvent.

Mass spectrum (MS) of BPM was recorded via a Bruker auto flex maX MALDI-TOF (Bruker Co., Germany).

Ultraviolet-visible (UV-Vis) absorption spectra of BPM and BPMNi were recorded on a Shimadzu UV 3600 Plus spectrometer.

Element contents of carbon (C), hydrogen (H) and nitrogen (N) in BPM and BPMNi were performed by a Vario EL III elemental analyzer (Elemental Co., Germany). Phosphorus (P) and nickel (Ni) elements were collected by an Avio200-ICP-OES inductively coupled plasma atomic emission spectroscopy (Perkin Elmer Co., America). Each sample was measured in 3 independent replicates.

Thermal gravimetric analysis (TGA) and corresponding differential thermogravimetric (DTG) curves of BPM, BPMNi, PA6 and PA6/BPMNi composites were determined with METTLER TOLEDO TGA 2 instrument (METTLER TOLEDO Co., Switzerland). About 5 mg of the sample was heated from 30 to 700 ^{o}C with a heating rate of 10 °C·min^{-1} under nitrogen and air atmosphere, respectively.

Differential scanning calorimetry (DSC) curves were conducted on a Perkin Elmer 4000 thermal analysis instrument (PerkinElmer Co., America) to investigate the melt-crystallization performance of PA6 and PA6/BPMNi composites. About 5 mg of the sample was heated from 30 to 280 ^{o}C and then kept at this temperature for 3 min to eliminate the thermal history. Then, the

sample was cooled to -50 °C and finally reheated to 280 °C at a rate of 10 °C·min^{-1}.

Degree of crystallinity (X_c) of PA6 and PA6/BPMNi composites was determined by using the following equation:

$$X_c = \Delta H_m / \Delta H_0 \quad (1)$$

where ΔH_m is the melting enthalpy of the sample and ΔH_0 (190.6 J·g^{-1})[1] was the melting enthalpy of fully crystalline PA6.

Relative viscosity (η_r) of sample was measured by employing an Ubbelohde viscometer according to ISO 307 standard. Each measurement was performed in 3 independent replicates. 0.5 g sample was dissolved in 50 mL sulfuric acid with concentration of 96%, and the flowability of the prepared solution was measured at 25.00 ± 0.01 °C. Number average molecular weight (M_n) of sample was determined by the following empirical equation:[2]

$$M_n = (\eta_r - 1) \times 11500 \quad (2)$$

Limiting oxygen index (LOI) tests of PA6 and PA6/BPMNi composites were carried out on a Zr-1 instrument (Shanfang Instrument Co., China) according to ASTM D2863. Each test was performed in 5 independent replicates, and the specimen size was 115 × 10 × 4 mm^3.

Vertically burning teat (UL-94) of PA6 and PA6/BPMNi composites were implemented by a CFZ-II burning tester (Jiangning Analysis Instrument Co., China) according to ASTM D3801. Each test was conducted in 5 independent replicates with a dimensional size of 125 × 13 × 3.2 mm^3.

Cone calorimetric measurements of PA6 and PA6/BPMNi composites were tested by a Fire Testing Technology cone calorimeter (FTT Co., England) according to ISO 5660 at a heat flux of 50 kW·m^{-2}. Each measurement was performed in 3 independent replicates, and the sample was prepared with a square geometry of 100 × 100 × 3 mm^3.

Thermogravimetric analysis-infrared spectrometry (TG-IR) measurement of PA6/BPMNi-3 was collected on a NETZSCH STA 449F5 analyzer (NETZSCH Co., Germany). About 5 mg sample was heated from 30 to 800 ^{o}C under a nitrogen atmosphere at a rate of 10 ^{o}C·min^{-1}. The temperatures of the transfer line and gas cell were both set at 260 °C.

Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) tests of PA6 and PA6/BPMNi-3 at the pyrolysis temperature of 700 ^{o}C were performed on a Shimadzu GC/MS-QP-2010 Ultra spectrometer (Shimadzu Co., Japan).

Scanning electron microscopy (SEM) images of the char residues images of PA6/BPMNi-3 after the cone calorimetric tests were performed through a VEGA3 TESCAN GMH/GMU instrument (TESCAN Co., Czech Republic).

Raman spectroscopies of the residual chars after the cone calorimetric tests of PA6 and PA6/BPMNi-3 were conducted on a DXR2 Raman spectrometer (Thermo Fisher Scientific Co., America) with a 532 nm laser line.

X-ray photoelectron spectroscopy (XPS) measurements of the residues after the cone calorimetric tests of PA6/BPMNi-3 were performed using an Escalab 250Xi spectrometer (Thermo Fisher Scientific Co., America) equipped with Al-Kα excitation radiation ($h\upsilon$ = 1361.0 eV).

2. Number average molecular weights of PA6 and PA6/BPMNi composites

Table S1 Relative viscosities (η_rs) and number average molecular weights (M_ns) of PA6 and PA6/BPMNi composites.

Samples	η_r	M_n (g·mol^{-1})
PA6	2.7	2.0×10^4
PA6/BPMNi-1	2.6	1.8×10^4
PA6/BPMNi-2	2.6	1.8×10^4
PA6/BPMNi-3	2.5	1.7×10^4

3. Raman spectra of the char residues of PA6 and PA6/BPMNi-3

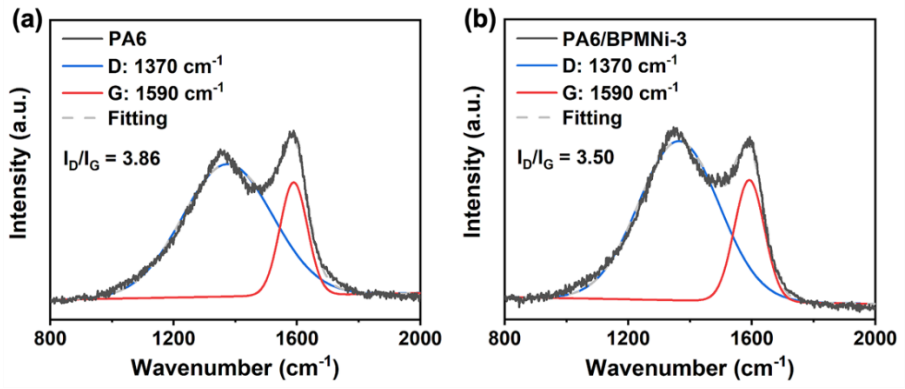
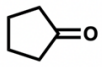
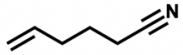
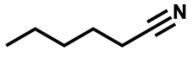
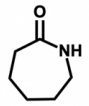
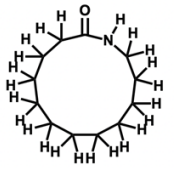
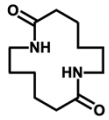
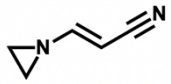
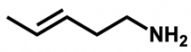
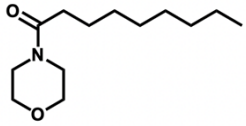


Figure S1 Raman spectra of the char residues of (a) PA6 and (b) PA6/BPMNi-3.

4. Py-GC/MS results of PA6 and PA6/BPMNi-3

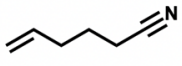
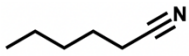
Table S2 Possible pyrolytic compounds of PA6 during heating at 700 °C.

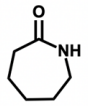
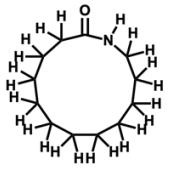
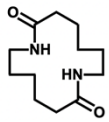
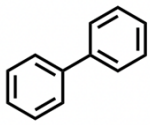
Peak	Retention Time (min)	m/z	Compounds [a]
1	1.70	44	CO_2
2	4.84	84	
3	6.01	95	
4	6.33	97	

5	11.88	113	
6	17.46	197	
7	20.67	226	
8	4.23	87	
9	7.00	94	
10	10.07	85	
11	22.01	227	

[a] Data come from NIST11s.library.

Table S3 Possible pyrolytic compounds of PA6/BPMNi-3 during heating at 700 °C.

Peak	Retention Time (min)	m/z	Compounds [a]
1	1.77	44	CO_2
2	4.87	84	
3	6.14	95	
4	6.36	97	

5	12.01	113	
6	17.50	197	
7	20.63	226	
12	12.59	154	

[a] Data come from NIST11s.library.

REFERENCES

1. K. Liu, Y. Li, L. Tao and R. Xiao, *RSC Advances*, 2018, **8**, 9261-9271.
2. S. Zhang, X. Fan, C. Xu, P. Ji, C. Wang and H. Wang, *Polymer*, 2020, **207**, 122890.