Introduction

Bio-based polypentamethylene adipate (PA56) is a novel industrial bio-based polymer, which is now mainly synthesized by polycondensation of bio-based 1,5-pentanediadime (PDA) and petroleum adipic acid. Compared with the traditional petroleum-based polyamides, bio-based PA56 is environmentally sustainable and has better performances such as higher moisture absorption, easier dyeing, and better melt-flowability, which are originated from its odd-numbered-carbon molecular structure. Naturally, PA56 can be widely used in textiles and engineering materials. However, the flammability of PA56 limits its application in the fields of household, electronic, electrical and automotive engineering, where high flame-retardancy is demanded[1]. Thus, it is an essential and urgent task to develop PA56 materials with good flame retardancy.

As is well known, blending and copolymerization are two classic methods to prepare flame-retardant materials. The blending method is convenience, efficiency, low-cost and easy to be processed. However, many flame retardants have poor dispersibility and weak compatibility in matrix materials, leading to significant deterioration of mechanical properties[2–5]. Besides, the flame retardant is easy to leach during processing, resulting in the reduction of flame retardancy[6, 7]. In contrast, reactive flame retardants, such as halogen, phosphorus, nitrogen, and silicon can be incorporated into the polymer chains through chemical bonds, endowing the material with inherent flame retardancy[8–11]. In addition, compared with the blending modification, the copolymerization modification has little
DDP is becoming a promising reactive flame retardant due to the high thermal stability and excellent flame-retardant properties, which has been successfully incorporated into polyester, polyamide and polyamide elastomer via copolymerization method[17–25]. However, although DDP exhibits the potential to improve the flame retardance of polymers, few investigations about its applications in PA56.

In this research, DDP was used as a phosphorus-containing reactive flame retardant to improve the flame retardance of PA56. The inherently flame-retardant PA56 copolymers (FRPA56s) were synthesized by melt polycondensation with PDA, AA and DDP as the monomer. The chemical structures were characterized by FTIR and NMR. The thermal properties were evaluated with DSC. The thermal degradation and flame behavior of FRPA56s were fully investigated by TGA, LOI, UL-94 and cone calorimeter tests. Subsequently, the condensed phase of FRPA56s after the cone calorimeter test was analyzed by SEM, Raman, FTIR and DDP is becoming a promising reactive flame retardant due to the high thermal stability and excellent flame-retardant properties, which has been successfully incorporated into polyester, polyamide and polyamide elastomer via copolymerization method[17–25]. However, although DDP exhibits the potential to improve the flame retardance of polymers, few investigations about its applications in PA56.

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Experimental

Materials

9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP), ethanol (EtOH), sulfuric acid (H₂SO₄), deuteriumsulfuric acid (D₂SO₄) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were purchased from TCI. 1,5-pentane diamine (PDA) and PDA-AA salt (salt of PDA and adipic acid (AA)) were obtained from Cathay Biotechnology Incorporation. All the chemicals were used without further purification.

Preparation of the PDA-DDP salt

DDP (17.313 g, 0.05 mol) was dissolved in ethanol (200ml) and transferred to a 500 ml three-necked flask equipped with a mechanical stirrer under 60 °C. After DDP was dissolved completely, stoichiometric PDA (5.109 g, 0.05 mol) was dissolved in ethanol to avoid PDA volatilization, and then slowly dropped into the ethanol solution of DDP. After all the PDA was added completely, the temperature was raised to 75 °C, and the reaction was continued for 3 h under reflux. PDA-DDP salt (white powder, 95% yield) was obtained by filtration, washed with ethanol and dried in a vacuum oven at 60 °C for 12 h.

Synthesis of flame-retardant PA56 copolymers (FRPA56s)

The FRPA56 samples containing 0.5, 0.7, 1.0 and 1.2 mol% DDP (labeled as PA56-0.5DDP, PA56-0.7DDP, PA56-1.0DDP and PA56-1.2DDP, respectively) were synthesized in a 300 ml autoclave (LB300, Shanghai LABE Instrument Co., Ltd, China) which was equipped with a nitrogen inlet and a mechanical stirrer. PDA-AA salt, PDA-DDP salt and deionized water (30 ml) were added to the autoclave according to the feeding molar ratio. The air in the autoclave was replaced with nitrogen three times before the reaction. Then the autoclave was heated to 220 °C and maintained for 1 h. The pressure was controlled at 2.0 MPa during this period. Subsequently, the temperature of the autoclave was increased to 270 °C, whereas the pressure was decreased to normal pressure. Then the reaction was continued for 1 h at 270 °C under vacuum (< 300 Pa) and FRPA56 was obtained after cooling. The preparation process of FRPA56s is shown in Scheme 1 and the composition of FRPA56s is summarized in Table S1.

Characterization

FTIR spectra were recorded on a Nicolet 8700 spectrometer with a diamond crystal attenuated total reflection (ATR) Smart accessory. Data was collected over 32 scans with a resolution of 4 cm⁻¹. Advanced ATR calibration and baseline correction were performed on data using Omnic software. 1H NMR and 31P NMR were acquired on Bruker Avance 600 MHz spectrometer. All the chemical shifts were referenced to TMS.

The crystallization and melting behavior of FRPA56s were performed on PerkinElmer DSC 4000 apparatus. The sample (~5 mg) was sealed in an aluminum pan and high purity nitrogen was used as the purging gas. The sample was firstly melted at 270 °C for 3 min to remove the thermal history, then cooled to 30 °C at 20 °C/min (cooling scan). After being held at 30 °C for 3 min, it was heated again to 270 °C at 20 °C/min (second heating scan). The peak maxima of the cooling and the second heating scans were taken as crystallization temperature (Tc) and the melt temperature (Tm), respectively, and the area of the peak as the crystallization enthalpies (ΔHc) and the melt enthalpies (ΔHm), respectively.

Thermal degradation behavior was evaluated using Mettler-Toledo TGA2 SF/1100 under nitrogen and air atmosphere. The heating rate was 10 °C/min from 30 °C to 700 °C and the purge flow of 50 mL/min. The UL94 vertical burning tests were conducted on CFZ-II burning tester according to ASTM E1354. Squared FRPA56s specimens of 115 mm × 10 mm × 3.2 mm were horizontally irradiated under a heat flux of 50 kW m⁻².

SEM was carried out on Hitachi Model S-4700 to visualize the morphology of FRPA56s residue char after cone calorimetric tests. Raman spectra of residue char were performed using a Renishaw Via-Reflex Raman spectrometer with a laser of 532 nm. X-ray photoelectron spectroscopy (XPS) of residue char were recorded on a Thermo Fisher Scientific EscaLab 250Xi system to obtain the element composition with an Al Kα radiation at 1486.8 eV.

The pyrolysis products of CEPPA, PA56 and PA56-1.2DDP at 350, 400, 450, 500 and 600 °C were obtained by TGA-GC/MS using the Mettler-Toledo TGA2 SF/1100,
which was linked to the Agilent 5977 gas chromatography-mass spectrometry (GC/MS).

Results and discussion

Structure analysis of PA56 and FRPA56s

The inherently FRPA56s were synthesized according to Scheme 1. The FTIR spectra of PA56 and FRPA56s are presented in Fig. 1. In the spectrum of PA56, the bands around 3300 and 3085 cm$^{-1}$ are associated with the stretching vibration of N-H of amide A and amide B, respectively. The peaks around 1642 cm$^{-1}$ correspond to the amide I bands arising from C=O stretch vibrations, while the peaks at 1548 cm$^{-1}$ are attributed to the amide II bands resulting from C-N stretch vibrations and N-H bending[26]. The FTIR spectra of FRPA56s are very similar to that of PA56 because of the low DDP content. In addition, in the range of 1740–1580 cm$^{-1}$ (the enlarged drawing in Fig. 1b), the peak at 1702 cm$^{-1}$ corresponds to the stretching vibration of C=O in DDP, which confirms the incorporation of DDP. 

![FTIR spectra of PA56 and FRPA56s](image)

![H NMR and 31P NMR spectra of PA56 and FRPA56s](image)
into the PA56 chain by the copolymerization\[18\]. Besides, the amide I band of FRPA56s shows a blue shift compared to PA56, indicating the strengthened interactions between molecular chains of FRPA56s. Furthermore, two shoulder peaks around 1253 and 1186 cm\(^{-1}\) arise from the gauche conformation of CH\(_2\)-NH in PA56, which indicates the presence of γ crystal form in PA56 and FRPA56s\[27\].

The \(^1\)H NMR spectra of PA56 and FRPA56s with deuteriosulfuric acid as solvent are displayed in Fig. 2a. The signals at 1.7 (a), 2.1 (b) and 3.8 (c) ppm are assigned to the methylene in PDA unit, the peaks at 3.0 (d) and 2.0 (e) ppm are assigned to the methylene in AA unit. The chemical shifts between 7.5 and 8.6 ppm (i) belong to the protons in the phosphaphenanthrene ring of DDP unit. The insert clearly shows the phosphaphenanthrene ring protons peaks of FRPA56s. In addition, as shown in Fig. 2b, two signals appear at 35.26 and 35.70 ppm in the \(^{31}\)P NMR spectrum of DDP, which might be triggered by the steric hindrance of phosphaphenanthrene group. The signals shift to 43.77 and 44.39 ppm in the \(^{31}\)P NMR spectrum of FRPA56 containing 1.2 mol% DDP. All results of FTIR, \(^1\)H NMR and \(^{31}\)P NMR confirm that DDP has been successfully incorporated into the PA56 backbone.

**Thermal properties and degradation behavior of PA56 and FRPA56s**

**The crystallization and melting behavior**

Figure 3 depicts the DSC cooling (a) and second heating (b) curves of PA56 and FRPA56s, and the results are summarized in Table 1. The crystallization temperature (T\(_c\)) of FRPA56s decreases after the first increase with the DDP content increasing and is higher than that of PA56, indicating that DDP acts as a nucleating agent in the crystallization process of FRPA56s and accelerates the crystallization rate of FRPA56s [28]. Notably, the increase of T\(_c\) for FRPA56 containing 1.2 mol% DDP is not obvious compared with PA56, which is due to the higher steric hindrance generated by the high content of DDP, restricting the movement of molecular chains in FRPA56s. In addition, The phosphaphenanthrene structure of DDP destroys the symmetry and regularity of molecular chains in FRPA56s, which restricts the arrangement of molecular chains into the lattice, resulting in the formation of thinner lamellae. Therefore, compared with PA56 (255 °C), the T\(_m\) of FRPA56s moves slightly towards 251 °C with the DDP content increased to 1.2 mol%. Furthermore, the crystallinity (X\(_c\)) of PA56-0.5DDP is almost the same as PA56, as listed in Table 1. As the increase of DDP content, the crystallinity shows a decreasing tendency as the symmetry and regularity of molecular chains are destroyed for FRPA56s.

| Sample         | T\(_c\)\(^a\) (°C) | T\(_m\)\(^b\) (°C) | \(\Delta H_m\)\(^b\) (J.g\(^{-1}\)) | X\(_c\)\(^c\) (%) |
|---------------|-----------------|----------------|-------------------|------------------|
| PA56          | 203             | 255            | 67                | 36               |
| PA56-0.5DDP   | 206             | 254            | 69                | 37               |
| PA56-0.7DDP   | 205             | 253            | 65                | 35               |
| PA56-1.0DDP   | 207             | 252            | 62                | 33               |
| PA56-1.2DDP   | 204             | 251            | 62                | 33               |

\(^{a}\)T\(_c\): the crystallization temperature determined in the cooling scan  
\(^{b}\)T\(_m\), \(\Delta H_m\): the melting temperature and the melting enthalpy were determined in the second heating scan, respectively  
\(^{c}\)X\(_c\): the crystallinity is determined by the equation: 

\[
X_c = \left( \frac{\Delta H_m}{\Delta H_m^0} \right) \times 100\% \quad (\Delta H_m^0 \text{ is } 188 \text{ J/g}[29])
\]

Fig. 3  DSC cooling curves (a) and second heating curves (b) of PA56 and FRPA56s
Thermal degradation behavior

TGA and derivative thermogravimetric (DTG) curves of PA56 and FRPA56s under nitrogen and air atmospheres are depicted in Fig. 4. The initial thermal decomposition temperature (T\textsubscript{5\%}), maximum decomposition temperature (T\textsubscript{max}), and residue char at 700 °C are summarized in Table 2. Under the nitrogen atmosphere, PA56 shows a typical one-stage degradation process with the T\textsubscript{5\%} at 394 °C and T\textsubscript{max} at 440 °C. All FRPA56s exhibit two primary thermal decomposition processes, indicating that the incorporation of DDP changes the degradation mechanism of PA56. Notably, as the DDP content increased from 0.5 to 1.2 mol %, the T\textsubscript{5\%} of FRPA56s decreased from 375 to 361 °C. The phenomenon is ascribed to the breakage of the P-O-C and O-P=O bonds in FRPA56s in advance, which releases flammable small molecules into the gas phase[18]. In addition, FRPA56s release phosphorus-containing radicals to capture H and OH radicals in the gas phase and generate phosphoric acid compounds which accelerate the degradation of FRPA56s at 403–411 °C (T\textsubscript{max,1}). As the temperature further increased to near 452 °C (T\textsubscript{max,2}), the amide fragments of FRPA56s occurs scission. Besides, the residue char of FRPA56s increases to 2.95% with the DDP content increased to 1.2 mol %, revealing that DDP promotes the formation of residue char.

Under the air atmosphere, the degradation behavior of FRPA56s is consistent with the nitrogen atmosphere. It includes the primary degradation process of FRPA56s between 415 and 404 °C and the secondary degradation process around 449 °C. In addition, a small shoulder peak appears near 568 °C (T\textsubscript{max,3}) in PA56 and FRPA56s. Furthermore, the residue char of PA56 under N\textsubscript{2} and air atmospheres are 1.89 and 0.00% while that of FRPA56s containing 1.2 mol% DDP under N\textsubscript{2} and air atmospheres are 2.95 and 0.85%, respectively. This phenomenon indicates that the residual char formed by PA56 at the lower temperature (T\textsubscript{max,1}) undergoes thermal-oxidative degradation at higher temperature (T\textsubscript{max,3}), while the phosphorus-containing compounds generated by FRPA56s at the lower temperature (T\textsubscript{max,1}) occurs dehydration and carbonization reactions at higher temperature (T\textsubscript{max,3})[30].

Flame retardant properties

The results of the UL94 vertical burning and LOI test are shown in Table 3. Although PA56 possesses self-extinguishing during combustion, it only reaches V-2 grade in the UL94 vertical burning test due to the melting droplets produced by PA56 easily igniting the absorbent cotton (Figure S3). However, the melting droplets of FRPA56s become fewer and smaller with DDP content increases. FRPA56 passes V-0 grade in the UL94 vertical burning test with only 1.0 mol% DDP. In addition, compared with PA56 (22.5%), the LOI value of FRPA56s increased to 28.8% with the DDP
content increased to 1.2 mol%, indicating that DDP is an efficient flame retardant for PA56.

Cone calorimetric tests are performed to assess the dynamic combustion behavior of PA56 and FRPA56s. The relevant combustion parameters to evaluate the fire disaster include the time to ignition (TTI), total heat release (THR), heat release rate (HRR), peak heat release rate (p-HRR), maximum average rate of heat emission (MARHE), total smoke release (TSR), CO production rate (COP), average effective heat of combustion (av-EHC), specific extinction area (SEA) and char residue are provided in Fig. 5; Table 4.

As shown in Fig. 5, PA56 burns rapidly after ignition with a TTI of 54 s, the p-HRR value of PA56 arrives at 1091 kW·m$^{-2}$ within 131 s (time to p-HRR) and the THR value of PA56 reaches 117 MJ·m$^{-2}$. Compared with PA56, the TTI and time to p-HRR of FRPA56-1.2DDP are shortened to 41 and 59 s, respectively, which is ascribed to the breakage of the P-O-C and O-P=O bonds in advance\[32\]. The p-HRR value of PA56-0.7DDP and PA56-1.2DDP reduces to 1009 and 713 kW·m$^{-2}$, with 8\% and 35\% decrements compared with PA56, respectively. THR shows a similar trend as p-HRR and those values of PA56-0.7DDP and PA56-1.2DDP decline to 98 and 95 MJ·m$^{-2}$ with the decrement of 16\% and 19\% compared to PA56, respectively. All results clarify that DDP is a valuable flame retardant as it significantly inhibits the total heat release of FRPA56s\[31\]. MARHE is defined as the peak of the cumulative heat emission divided by time, which is a good measure of the propensity for fire development under real-scale conditions, playing an important role as a fire safety parameter. As shown in Table 4, the MARHE value of PA56 reaches 466 MJ·m$^{-2}$, while the MARHE values of PA56-0.7DDP and PA56-1.2DDP decrease to 444 and 416 kW·m$^{-2}$, respectively, indicating that the overall fire performance of PA56 has improved.

SEA and TSR reflect the smoke release amount during the combustion. Compared with PA56, the SEA and TSR value of PA56-1.2DDP increases to 197 m$^2$·kg$^{-1}$ and 1218 m$^2$·m$^{-2}$ from 71 m$^2$·kg$^{-1}$ and 481 m$^2$·m$^{-2}$ (Fig. 5c; Table 4), respectively, indicating that FRPA56s produce more aromatic volatiles during combustion. Av-EHC reveals the combustible degree of volatiles in the gas phase. As shown in Table 4, compared with PA56 (31 MJ·Kg$^{-1}$), the av-EHC value of PA56-1.2DDP reduces to 24 MJ·Kg$^{-1}$, revealing that the combustion degree of FRPA56s weakens. The p-COP value rises to 0.014 g/s for PA56-1.2DDP from 0.007 g/s for PA56, which suggests that PA56-1.2DDP burns incompletely compared with PA56. FRPA56s releases PO, PO$_2$ and phenyl radicals to capture H and OH radicals in the flame zone by quenching effect, leading to incomplete combustion of FRPA56s\[33\]. Notably, the residual char slightly increased to 0.97\% with the DDP content of 1.2 mol\%, which is consistent with TGA results.

### Table 2 TGA data of PA56 and FRPA56s in nitrogen and air atmosphere

| Sample        | $\mathrm{T_{5\%\ a}}$ (℃) | $\mathrm{T_{\text{max} b}}$ (℃) | $\mathrm{T_{\text{max} c}}$ (℃) | $\mathrm{T_{\text{max} d}}$ (℃) | Char (%) |
|---------------|-----------------------------|---------------------------------|---------------------------------|---------------------------------|-----------|
| N$_2$         |                             |                                 |                                 |                                 |           |
| PA56          | 394                         | 380                             | 440                             | 550                             | 1.89      |
| PA56-0.5DDP   | 375                         | 374                             | 411                             | 494                             | 0.62      |
| PA56-0.7DDP   | 373                         | 369                             | 411                             | 497                             | 0.78      |
| PA56-1.0DDP   | 368                         | 367                             | 409                             | 477                             | 0.85      |
| PA56-1.2DDP   | 361                         | 366                             | 404                             | 447                             | 0.85      |
| Air           |                             |                                 |                                 |                                 |           |
| PA56          | 420                         | 411                             | 451                             | 565                             | 0.00      |
| PA56-0.5DDP   | 411                         | 411                             | 451                             | 565                             | 0.00      |
| PA56-0.7DDP   | 411                         | 411                             | 451                             | 565                             | 0.00      |
| PA56-1.0DDP   | 409                         | 409                             | 451                             | 565                             | 0.00      |
| PA56-1.2DDP   | 404                         | 404                             | 451                             | 572                             | 0.00      |

\(\mathrm{T_{5\%\ a}}\): the decomposition temperature corresponds to 5\% mass loss

\(\mathrm{T_{\text{max} b}}\): the decomposition temperature corresponds to the maximum mass loss rate

\(\mathrm{T_{\text{max} c}}\): the decomposition temperature corresponds to the maximum mass loss rate

\(\mathrm{T_{\text{max} d}}\): the decomposition temperature corresponds to the maximum mass loss rate

\(\mathrm{Char\ at\ 700\ ℃}\): the decomposition temperature corresponds to 5\% mass loss
Table 3  The UL-94 vertical burning results and LOI values of PA56 and FRPA56s

| Sample         | $t_1^a$ (s) | $t_2^a$ (s) | Melting droplets amount$^c$ | Ignite cotton or not | UL94 rating | LOI value (%) |
|----------------|-------------|-------------|----------------------------|---------------------|--------------|---------------|
| PA56           | 12.1        | 6.3         | 2                          | yes                 | V-2          | 22.5±0.2      |
| PA56-0.5DDP    | 5.3         | 3.5         | 1.3                        | yes                 | V-2          | 23.4±0.1      |
| PA56-0.7DDP    | 4.7         | 3.3         | 0.6                        | yes                 | V-2          | 24.2±0.1      |
| PA56-1.0DDP    | 1.5         | 3.2         | 0.5                        | no                  | V-0          | 26.4±0.2      |
| PA56-1.2DDP    | -           | 5.4         | 0.3                        | no                  | V-0          | 28.8±0.1      |

$^a$ $t_1$: time of self-extinguishing after the first ignition;  
$^b$ $t_2$: time of self-extinguishing after the second ignition;  
$^c$ Melting droplets amount: average value of the melted droplets produced by five effective splines;  
$^d$ Not ignited

Table 4  Combustion results of PA56 and FRPA56s obtained from cone calorimeter test

| Sample         | TT1 (s) | THR (MJ·m$^{-2}$) | p-HRR (kW·m$^{-2}$) | TSR (m$^2$·m$^{-2}$) | MARHE (kW·m$^{-2}$) | p-COP (g·s$^{-1}$) | SEA (m$^2$·kg$^{-1}$) | av-EHC (MJ·kg$^{-1}$) | Residual char (%) |
|----------------|---------|-------------------|---------------------|----------------------|---------------------|-------------------|----------------------|---------------------|------------------|
| PA56           | 54      | 117               | 1091                | 481                  | 466                 | 0.007             | 71                   | 31                  | 0.00             |
| PA56-0.7DDP    | 51      | 98                | 1099                | 999                  | 444                 | 0.014             | 189                  | 26                  | 0.50             |
| PA56-1.2DDP    | 41      | 95                | 713                 | 1218                 | 416                 | 0.014             | 197                  | 24                  | 0.97             |

Fig. 5  Cone calorimetric results of PA56 and FRPA56s: (a) THR, (b) HRR, (c) TSR and (d) COP
Analysis of the condensed phase

Figure 6 summarizes the digital photographs, SEM micrographs and Raman spectra of residual char layers after cone calorimetric tests for PA56, PA56-0.7DDP and PA56-1.2DDP. The residual char of PA56 after combustion is negligible while that of FRPA56 increases with DDP content. The SEM images further perform the details of the microscopic surface. PA56 forms porous and fragile char layers with a smooth surface, while the char layers of FRPA56s are compact. In addition, a plentiful of corrugated folds are found on the surface, which serves as a skeleton to strengthen the residual char, interrupting the transfer of heat and oxygen between the flame and unburned part[28]. At higher magnification (10000x), the carbon spheres are observed on the surface of residual char, and their amounts extend with DDP content increases. These microstructures prove that DDP has undergone chemical reactions (dehydration and carbonization) during combustion[15].

The compactness is further quantitatively compared by the integral area ratio $I_D/I_G$ (at 1372 and 1585 cm$^{-1}$) in Raman spectra. The larger $I_D/I_G$, the smaller crystallite size and the denser the char layers[34]. The $I_D/I_G$ value increases in the following order: PA56 (2.95)<PA56-0.7DDP (3.97)<PA56-1.2DDP (4.51), indicating that DDP promotes the formation of a denser char layer with a smaller microcrystalline structure, which is consistent with the SEM results.

Figure 7a shows the FTIR of the residual char after the cone calorimeter test for PA56 and FRPA56s. Compared with PA56, FRPA56s emerge phosphorus-containing groups peaks at 1216, 1150, 1120, 1092 and 1055 cm$^{-1}$, which is ascribed to phosphorous /hypophosphorous acid derivatives. The peak at 1216 cm$^{-1}$ is related to R(OR)(OH)=P-O group, the band around 1155 cm$^{-1}$ is attributed to R(OH)$_2$P=O group, the signal at 1120 cm$^{-1}$ derived from the stretching vibrations of P-O-C and two peaks at 1092 and 1055 cm$^{-1}$ correspond to the P-OH bond[35]. Those results further reveal that DDP generates the phosphoric acid and hypophosphorous acid derivatives during combustion. The phosphoric acid and hypophosphorous acid derivatives further react (dehydration and carbonization) with polyamide to form the phosphorus-containing dense char layers with polyaromatic structure. The char layers cover the surface.

**Fig. 6** The digital photographs, SEM micrographs and Raman spectra of residual char layers after cone calorimetric tests for PA56, PA56-0.7DDP and PA56-1.2DDP

**Fig. 7** FTIR spectra (a), XPS survey spectra (b), high-resolution spectra of C1s (c), O1s (d), and P2p (e) regions of residual char for PA56 and FRPA56s after cone calorimeter tests
of the matrix, isolating heat and oxygen, preventing further pyrolysis of the PA56 and terminating the combustion of PA56 eventually[13].

Figure 7b presents the XPS survey spectra of PA56, PA56-0.7DDP and PA56-1.2DDP. The C, N and O elements on the surface of the sample are detected, and the P element appears in the residue char of PA56-0.7DDP and PA56-1.2DDP[28, 36]. To further analyze the chemical structure of residue char, the corresponding C1s, O1s, and P2p spectra of PA56 and PA56-1.2DDP are depicted in Fig. 7c-e. The C1s peaks of PA56 and PA56-1.2DDP are spilled into four characteristic bands at 286.4, 285.6, 284.9 and 284.4 eV, which are designated to the C = O, C-N, C-O and C-C, respectively[36]. In the O1s spectra of PA56, two peaks around 533.6 and 531.0 eV is ascribed to C-O and C = O. The residue of PA56-1.2DDP exhibits an additional peak at 532.4 eV, which corresponds to P-O[28]. For the P2p spectrum of PA56-1.2DDP, two peaks occur at 134.5 and 133.5 eV are attributed to P-O-C and O-P = O groups of phosphoric /hypophosphorous acid and its derivatives, which coincides with FTIR results, further demonstrating that DDP plays a flame retardant role in the condensed phase[36].

Analysis of the gas phase

The total ion chromatogram of DDP at 350, 400, 450, 500 and 600 °C are shown in Fig. 8a, along with the detailed pyrolysis products in Fig. 8d. As shown in Fig. 8a and d, the main pyrolytic products of DDP are 6-heptenoic acid (d6), o-hydroxybiphenyl (d8), fluorene (d9), 9-methyl-9 h-fluorene (d10), 2-(1-phenylethyl) phenol (d11), 1-phenoxo-2-(2-propen-1-yl) benzene (d12) and triphenylene (d13). O-hydroxybiphenyl and fluorene are formed by the cleavage of the P-C bond in DDP, accompanied by the release of PO, PO2 and phenyl radicals during the pyrolysis process. Subsequently, o-hydroxybiphenyl and fluorene continue to cleave, forming stable gas products containing phenyl groups. Figure 9 depicts the pyrolysis process diagram of DDP.

Figure 8b and c show the total ion chromatogram of PA56 and PA56-1.2DDP. The corresponding major gaseous products are presented in Fig. 8e and f, respectively. The α-methyl next to the amide bond and amino group of PA56 is easily scissile, leading to decarboxylation, deamination, alkylation and acylation reaction[37]. The main pyrolysis products of PA56 are cyclopentanone (e1) and pyridine (e2) accompanied by CO2 and NH3[37]. The cyclopentanone and pyridine further capture the molecule radicals (methyl, ethyl and pentyl radicals) forming cyclopentanone derivatives (e3, e4, e5, e7, e8, e10) and nitrogen-containing compounds (e6, e9, e10, e11). Some characteristic pyrolysis products of PA56, such as cyclopentanone (e1/f1), [1,1’-bicyclopentyl]-2-one (e5/f5), pyrrolidine(e6/f6), are also detected in the chromatogram of PA56-1.2DDP, indicating that FRPA56s also releases nonflammable gas (CO2 and NH3) by decarboxylation and deamination of pentamethylene adipamide structure. In addition, methylbenzene (d1/f2) and o-hydroxybiphenyl (d8/f8) generated from DDP is also found in the chromatogram of PA56-1.2DDP. The result indicates that PA56-1.2DDP releases PO and Ph radicals during the thermal pyrolysis process to capture H and OH and other radicals, interrupting the free radicals chain reaction and exothermic process of PA56-1.2DDP by quenching effect, thereby suppressing the combustion of FRPA56s in the gases phase. Besides, some novel nitrogen-containing pyrolysis substances, such as f9, f10, f11 and f12, are also found in the chromatogram of PA56-1.2DDP. The nonflammable gases (CO2, NH3 and nitrogen-containing compounds (f9, f10, f11 and f12)) formed from the pyrolysis of PA56-1.2DDP dilute the concentration of combustible volatiles, further depressing the combustion degree of PA56.
Flame-retardant mechanism of FRPA56s

Based on the above-mentioned degradation and flame behaviors analysis, the flame-retardant mechanisms of DDP incorporated FRPA56s are proposed. As shown in Fig. 10, FRPA56 releases PO, PO$_2$ and phenyl radicals in the gas phase, which capture H and OH radicals in the flame zone, interrupting the exothermic processes by quenching effect, suppressing the combustion of polymer in the gases phase. In addition, the nonflammable gases dilute the concentrations.
of flammable gases and oxygen in the gas phase and take away the heat during combustion. In the condensed phase, FRPA56s form the phosphorus-containing dense char layers with polyaromatic structure during combustion, the dense char layers cover the surface of the matrix, isolating heat and oxygen, preventing further pyrolysis of the PA56 and terminating the combustion of PA56 eventually.

Conclusions

In summary, the inherently flame-retardant PA56 copolymers are successfully prepared with the simple introduction of 9,10-dihydro-10-[2,3-di(hydroxy carbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP) unit. V-0 grade is achieved for bio-based PA56 by the incorporation of only 1.0 mol% DDP in the UL94 vertical burning test, which confirms that the DDP copolymerization strategy is effective to improve flame retardancy of bio-based PA56. The pyrolysis products in both condensed and gas phases were analyzed with SEM, Raman, FTIR, XPS and TGA-GC/MS for FRPA56s. Based on the analysis, the flame-retardant mechanism of FRPA56 was proposed: (i) FRPA56s can release PO, PO₂ and Ph radicals as free radical scavenging agents, inhibiting the combustion through the quenching effect in the gas phases; (ii) the nonflammable gases generated by FRPA56s, such as CO₂, NH₃ and nitrogen-containing compounds, reduce the concentrations of flammable gases and oxygen in the gas phase and take away the heat during combustion; (iii) FRPA56s form dense char layers during combustion cover the surface of the matrix, isolating heat and oxygen, preventing further pyrolysis of the PA56.

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Conflict of interest The authors declare no competing financial interest.

References

1. Xiong LK, Qin BB, Liu XC (2017) Bio-based flame retardant polyamide 56 and its preparation method. China
2. Liu XF, Liu BW, Luo X, Guo DM (2020) A novel phosphorus-containing semi-aromatic polyester toward flame retardancy and enhanced mechanical properties of epoxy resin.Chem Eng J380
3. Wang P, Chen L, Xiao H (2019) Flame retardant effect and mechanism of a novel DOPO based tetrazole derivative on epoxy resin. J Anal Appl Pyrol 139:104–113
4. Li YY, Liu K, Xiao R (2017) Preparation and characterization of flame-retarded polyamide 66 with melamine cyanurate by in situ polymerization. Macromol Res 25(8):779–785
5. Sun QH, Wang YH, Wei JG, Shen YS, Chen X, Zhang BC, Song XF (2021) Synthesis of novel EDPP for inflaming retarding PLLA.Polym Degrad and Stab 186
6. Kanat M, Eren T (2019) Synthesis of phosphorus-containing flame retardants and investigation of their flame retardant behaviour in textile applications.J Appl Polym Sci136(36)
7. Wang R, Wang WQ, Wang FH, Zhang AY, Zhang X, Wang DY (2021) Construction of nano-multilayer coatings on copolyester fabrics using UV-grafting mediated layer-by-layer self-assembly for improved anti-droplet and flame retardant performance.Polym Degrad and Stab183
8. Fan S, Yuan RC, WU DQ, Wang XL, Yu JY, Li FX (2019) Sili-con/nitrogen synergistically reinforced flame-retardant PA6 nanocomposites with simultaneously improved anti-dripping and mechanical properties. RSC Adv 9(14):7620–7628
9. Wang H, Liu Q, Zhao X, Jin Z (2021) Synthesis of reactive DOPO-based flame retardant and its application in polyurethane elastomers.Polym Degrad and Stab183
10. Ma Y, Gong X, Liao C, Geng X, Wang C, Chu F (2018) Preparation and Characterization of DOPO-ITTA Modified Ethyl Cellulose and Its Application in Phenolic Foams.Polymers10(10)
11. Lu SY, Hamerton I (2002) Recent developments in the chemistry of halogen-free flame retardant polymers. Prog Polym Sci 27(8):1661–1712
12. Liu K, Li Y, Tao L, Liu C, Xiao R (2019) Synthesis and characterization of inherently flame retardant polyamide 6 based on a phosphine oxide derivative. Polym Degrad and Stab 163:151–160
13. Ao X, Du Y, Yu D, Wang W, Yang WZ, Sun B, Zhu MF (2020) Synthesis, characterization of a DOPO-based polymeric flame retardant and its application in polyethylene terephthalate. Pro Nat Sci 30(2):200–207
14. Lu P, Zhao ZY, Xu BR, Li YM, Deng C, Wang YZ (2020) A novel inherently flame-retardant thermoplastic polyamide elastomer. Chem Eng J379
15. Zhang SM, Fan XS, Xu CC, Ji P, Wang CS, Wang HP (2020) An inherently flame-retardant polyamide 6 containing a phosphorus group prepared by transesterification polymerization.Polymer207
16. Wang LS, Kang HB, Wang SB, Liu Y, Wang R (2007) Solubilities, stabilities and flame retardance behaviour of phosphorus-containing flame retardants and copolymer. Fluid Phase Equilibria 258(2):99–107
17. Mourgas G, Giebel E, Bauch V, Schneck T, Unold J, Buchmeiser MR (2019) Synthesis of intrinsically flame-retardant copolyamides and their employment in PA6-fibers. Polym Adv Technol 30(11):2872–2882
enhancement of fire safety and crystallization rate of poly(lactic acid). Chem Eng J 421
29. Morales-Gámez L, Soto D, Franco L, Puiggali J (2010) Brill transition and melt crystallization of nylon 56: An odd–even polyamide with two hydrogen-bonding directions. Polymer 51(24):5788–5798
30. Luo XL, Li ZY, Shen JY, Liu L, Chen H, Hu ZQ, Krucinska I, Yao JM (2022) A facile strategy to achieve efficient flame-retardant cotton fabric with durable and restorable fire resistance. Chem Eng J 430
31. Zhang JH, Mi XQ, Chen SY, Xu ZJ, Zhang DH, Miao MH, Wang JS (2020) A bio-based hyperbranched flame retardant for epoxy resins. Chem Eng J 381
32. Zhang PK, Fan HJ, Tian SQ, Chen Y, Yan J (2016) Synergistic effect of phosphorus-nitrogen and silicon-containing chain extenders on the mechanical properties, flame retardancy, and thermal degradation behavior of waterborne polyurethane. RSC Adv 6(76):72409–72422
33. Wang P, Cai Z (2017) Highly efficient flame-retardant epoxy resin with a novel DOPO-based triazole compound: Thermal stability, flame retardancy and mechanism. Polym Degrad and Stab 137:138–150
34. Fu T, Wang XL, Wang YZ (2021) Flame-responsive aryl ether nitrile structure towards multiple fire hazards suppression of thermoplastic polyester. J Hazard Mater 403:123714
35. Schartel B, Perret B, Dittrich B, Ciesielski M, Kramer J, Muller P, Altstadt V, Zang L, Doring M (2016) Flame Retardancy of Polymers: The Role of Specific Reactions in the Condensed Phase. Macromol Mater Eng 301(1):9–35
36. Li J, Zhu HF, Li J, Fan XY, Tian XY (2011) Thermal Degradation Behaviors of Phosphorus-Silicon Synergistic Flame-Retardant Copolyester. J Appl Polym Sci 122(3):1993–2003
37. Zhang C, Huang JY, Liu SM, Zhao JQ (2011) The synthesis and properties of a reactive flame-retardant unsaturated polyester resin from a phosphorus-containing diacid. Polym Advan Techn 22(12):1768–1777
38. Li J, Zhu HF, Li J, Fan XY, Tian XY (2011) Thermal Degradation Behaviors of Phosphorus-Silicon Synergistic Flame-Retardant Copolyester. J Appl Polym Sci 122(3):1993–2003
39. Yang TT, Gao YB, Mutua FN, Hu HM, Liu XC, Zheng Y, Wang XL, He Y (2020) Effect of temperature on hydrogen bond of bio-based polyamide 56. J Donghua Univ (Nat Sci) 46(2):237–242
40. Yang TT, Gao YB, Wang XL, Ma BM, He Y (2021) Hydrogen bonding and crystalline structure of bio-based PA56. Polymer 237
41. Liu LB, Xu Y, Pan Y, Xu MJ, Di YF, Li B (2021) Facile synthesis of an efficient phosphonamide flame retardant for simultaneous enhancement of fire safety and crystallization rate of poly(lactic acid). Chem Eng J 421
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