A strategy to achieve the inherently flame-retardant PA56 by copolymerization with DDP

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Abstract

As a bio-based polyamide, PA56 is restricted in many fields due to its flammability. In this research, flame-retardant PA56 copolymers (FRPA56s) were designed and successfully synthesized with the introduction of 9,10-dihydro-10-[2,3-di(hydroxy carbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP) unit. The thermal properties, thermal degradation and flame behavior of the resultant copolymer were investigated by DSC, TGA, LOI, UL-94 and cone calorimeter tests, respectively. Compared to PA56, the peak value of heat release rate and total heat release of FRPA56 containing 1.2 mol% DDP decrease by 35 % and 19 %, respectively, indicating the high flame-retardant efficiency of DDP. It is also found that FRPA56 with only 1.0 mol% DDP passes V-0 grade in the UL-94 test while its thermal performance is almost the same as homopolymer PA56. The pyrolysis products in both the condensed and gas phases were further systematically analyzed by SEM, Raman, X-ray photoelectron spectroscopy and TGA-GC/MS. The flame-retardant mechanism was also proposed for FRPA56s.

1. Introduction

PA56 is a bio-based polyamide by Cathay Biotechnology Incorporation from bio-based 1,5-pentanediamine (PDA). Compared with the traditional petroleum-based polyamides, 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 effect on the performance of polymers[12]. Thus, reactive flame retardants have become the trend to improve flame resistance.

Halogen flame retardants are widely used as reactive flame retardants due to its high efficiency and low cost. However, halogen-containing flame retardants have been severely restricted in the past decades as it release toxic gases such as dibenzo-*p*-dioxin and hydrogen halide during combustion, which is harmful to the environment[13]. Organophosphorus-based flame retardants, such as 2-carboxyethyl(phenyl) phosphinic acid (CEPPA), 4,4'-(phenylphosphinylidene) bis[benzoic acid] (BCPPO) and 9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP), usually have the

characteristics of low toxicity, less smoke, environmental benignity and highly efficient flame resistance. Based on these properties, they have been considered as the alternative of halogen-free flame retardants[14-16]. Among them, DDP is becoming a promising reactive flame retardant due to the higher thermal stability and has been successfully incorporated into polyester, polyamide and polyamide elastomer through copolymerization[17-25].

As a novel polyamide, few investigations were performed on the flame-retardant PA56 copolymers (FRPA56s). In this research, DDP was used as a reactive flame retardant to improve the flame retardance of PA56. The inherently FRPA56s were synthesized by melt polycondensation of PDA, AA and DDP. 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 cone calorimeter test was analyzed by SEM, Raman, FTIR and XPS. The pyrolysis behaviors of FRPA56s were monitored by TGA-GC/MS. Based on these results, the flame-retardant mechanism was proposed for FRPA56s.

2. Experimental

2.1 Materials

9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide (DDP), ethanol (EtOH), sulfuric acid (H_2SO_4), deuteriosulfuric acid (D_2SO_4) 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.

2.2 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 slowly dropped. After all the PDA was added, the temperature was raised to 75 °C, and the reaction was continued for 3 hours 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.

2.3 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 into 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.

2.4 Characterization

FTIR spectroscopy was collected on a Nicolet 8700 spectrometer by the attenuated total reflection (ATR) method with 32 scans at a spectral resolution of 4 cm⁻¹. ¹H and ³¹P-NMR were acquired on Bruker Avance 600 MHz spectrometer.

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 minutes, 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 (T_c) and the melt temperature (T_m), respectively, and the area of the peak as the crystallization enthalpies (ΔH_c) and the melt enthalpies (ΔH_m), 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 UL-94 vertical burning tests were conducted on CFZ-II burning tester according to ASTM D3801 with specimen dimensions of 130 mm × 13 mm × 3.2 mm. The limiting oxygen index (LOI) values of FRPA56s were estimated on ZR-1 instrument in terms of ASTM D2863 with the specimen dimensions of 115 mm × 10 mm × 4 mm. The cone calorimetric tests were assessed using a VOUCH-6810 cone calorimeter following ASTM E1354. Squared FRPA56s specimens of 100 mm × 100 mm × 3 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 K α 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).

3. Results And Discussion

3.1. Structure analysis of PA56 and FRPA56s

The FTIR spectra of PA56 and FRPA56s are presented in Figure 1a. As shown in Figure 1a, the FTIR spectra of FRPA56s are very similar to PA56 due to the low content of DDP. 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 1510 cm^{-1} are attributed to the amide II bands resulting from C-N stretch vibrations and N-H bending[26]. In addition, two shoulder peaks around 1253 and 1186 cm^{-1} arise from the gauche conformation of the $\text{CH}_2\text{-NH}$ of PA56, which indicates the presence of g crystal form in PA56 and FRPA56s[27]. Notably, in the range of 1740-1580 cm^{-1} (Figure 1b), the peak at 1702 cm^{-1} corresponds to the C=O absorption band ($\nu_{\text{C=O}}$) of DDP, confirming the incorporation of DDP into the PA56 chain by the copolymerization[18]. Moreover, compared with PA56, the amide I bands of FRPA56s show a blue-shift, indicating the strengthened interactions between molecular chains [27].

The $^1\text{H-NMR}$ spectra of PA56 and FRPA56s with deuteriosulfuric acid as solvent are displayed in Figure 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 (i) of FRPA56s. Furthermore, $^{31}\text{P-NMR}$ spectrum of DDP exhibits two signals at 36.59 and 36.03 ppm, as shown in Figure 2b. For PA56-1.2DDP, the P proton signals are observed at 46.54 and 47.19 ppm instead of 36.59 and 36.03 ppm, indicating the introduction of DDP monomers in copolymers. All the results of FTIR, $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$ confirm that DDP has been successfully incorporated into the PA56 backbone.

3.2. Thermal properties and degradation behavior of PA56 and FRPA56s

3.2.1 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 is higher than PA56, indicating that DDP acts as a nucleating agent in the crystallization process[28]. The result is consistent with the FTIR. Compared with PA56 (255 $^{\circ}\text{C}$), T_m of FRPA56s ($\approx$ 251 $^{\circ}\text{C}$) moves slightly towards lower temperatures. This phenomenon is caused by the phosphaphenanthrene structure of DDP, which destroys the symmetry and regularity of molecular chains, resulting in the reduce of T_m for FRPA56s. Furthermore, the crystallinity 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.

Table 1. The thermal properties of PA56 and FRPA56s

Sample	T_c^a (°C)	T_m^b (°C)	ΔH_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 , ΔH_m : the melting temperature and the melting enthalpy determined in the second heating scan, respectively.

^c X_c : the crystallinity is determined by the equation: (is 188 J/g[29]).

3.2.2. Thermal degradation behavior

TGA and derivative thermogravimetric (DTG) curves of PA56 and FRPA56s under nitrogen and air atmospheres are depicted in Figure 4. The initial thermal decomposition temperature ($T_{5\%}$), maximum decomposition temperature (T_{max}) and residue char at 700 °C are summarized in Table 2. Under the nitrogen atmosphere, the $T_{5\%}$ and T_{max} of PA56 are determined to be 394 and 440 °C, respectively. With the incorporation of DDP, the $T_{5\%}$ and T_{max} of all FRPA56s are lower than PA56, which is primarily related to the degradation of P-O-C and O-P=O bonds in DDP. This phenomenon has been observed in another phosphorus-containing polyamide[18]. Fortunately, the FRPA56s still possess relatively good thermal stability. In addition, all FRPA56s exhibit two major decomposition process (Figure 4), which is different from PA56. The first stage of decomposition occurs in the temperature range of 403-411 °C, it is related to the degradation of phosphorus-containing compounds. The second stage of decomposition occurs around 452 °C, which generates from the amide fragments (Table 3). The residue char of PA56-1.2DDP increases to 2.95 %, 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. Furthermore, it is noteworthy that a small shoulder peak

appears near 568 °C ($T_{\max,3}$) in PA56 and FRPA56s. The peak originates from the catalyzes dehydration of phosphoric acid compounds, which are produced in the first stage of decomposition [30].

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

Sample	$T_{5\%}^a$ (°C)		$T_{\max1}^b$ (°C)		$T_{\max2}^b$ (°C)		$T_{\max3}^b$ (°C)	Char ^c (%)	
	N ₂	Air	N ₂	Air	N ₂	Air	Air	N ₂	Air
PA56	394	380	440	452	-	-	550	1.89	0.00
PA56-0.5DDP	375	374	411	415	451	449	565	1.94	0.62
PA56-0.7DDP	373	369	411	411	451	449	568	2.52	0.78
PA56-1.0DDP	368	367	406	409	453	447	565	2.64	0.85
PA56-1.2DDP	361	366	403	404	452	447	572	2.95	0.85

^a $T_{5\%}$: the decomposition temperature corresponds to 5% mass loss.

^b $T_{\max}$: the decomposition temperature corresponds to the maximum mass loss rate.

^c Char at 700 °C.

3.3. Flame behavior of PA56 and FRPA56s

3.3.1 Flame retardant properties

The results of the UL-94 and LOI test are shown in Table 3. Although PA56 possesses self-extinguishing during combustion, it only reaches V-2 in the UL-94 test due to the melting droplets easily igniting absorbent cotton. However, the melting droplets of FRPA56s become fewer and smaller with DDP content increases. FRPA56 passes V-0 in the UL-94 test with only 1.0 mol% DDP, indicating that DDP is an efficient flame retardant for PA56. DDP destroys the regularity of the PA56 segment, leading to the melt fluidity of PA56 increases. After igniting, the melted droplets quickly take away the heat of the spline surface, leading to the temperature decreasing of FRPA56s surface. Besides, DDP releases PO, PO₂ and phenyl radicals during pyrolysis, which interrupt the exothermic processes by quenching effect, suppressing the combustion of polymer in the gases phase[31]. The increase of LOI value for FRPA56s is not significant, further revealing that DDP mainly takes away the heat and releases phosphorous radicals in the gas to improve the flame retardant performance of PA56.

Table 3. The UL-94 vertical burning results and LOI values of PA56 and FRPA56s

Sample	UL-94 vertical burning test			
	melted droplets amount	ignite cotton or not	rating	LOI value (%)
PA56	2	yes	V-2	21.4
PA56-0.5DDP	1.3	yes	V-2	20.7
PA56-0.7DDP	0.6	yes	V-2	20.5
PA56-1.0DDP	0.5	no	V-0	21.2
PA56-1.2DDP	0.3	no	V-0	21.9

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), heat release rate (HRR), peak heat release rate (p-HRR), total heat release (THR), 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 Figure 5 and Table 4. As shown in Figure 5, PA56 burns rapidly after ignition with a TTI of 54 s, the p-HRR value of PA56 arrives $1091 \text{ kW}\cdot\text{m}^{-2}$ within 131 s (time to p-HRR) and the THR value of PA56 reaches $117 \text{ MJ}\cdot\text{m}^{-2}$. Compared with PA56, the TTI and time to p-HRR of FRPA56-1.2DDP are shortened to 41 and 59 s, respectively, which ascribe to the pyrolysis of DDP[32]. The p-HRR value of PA56-0.7DDP and PA56-1.2DDP reduces to 1009 and $713 \text{ kW}\cdot\text{m}^{-2}$, 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 $\text{MJ}\cdot\text{m}^{-2}$ with the decrement of 16 % and 19 % compared to PA56, respectively. All results clarify that DDP act as a valuable flame retardant since it significantly inhibit the total heat release of FRPA56s.

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 $197 \text{ m}^2\cdot\text{kg}^{-1}$ and $1218 \text{ m}^2\cdot\text{m}^{-2}$ from $71 \text{ m}^2\cdot\text{kg}^{-1}$ and $481 \text{ m}^2\cdot\text{m}^{-2}$ (Figure 5c and Table 4), respectively, indicating that FRPA56s produce more smoke during combustion. Av-EHC reveals the burning degree of combustible volatiles in the gas phase. The av-EHC value of PA56-1.2DDP reduces from 31 to $24 \text{ MJ}\cdot\text{Kg}^{-1}$ (Table 4), revealing that the FRPA56 combustion degree weakens with the incorporation of DDP. The p-COP value rises from 0.007 g/s for PA56 to 0.014 g/s for PA56-1.2DDP (Table 4), which suggests that PA56-1.2DDP burns incompletely compared with PA56. The PO, PO₂ and phenyl radicals generated by DDP can 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 4. Combustion results of PA56 and FRPA56s obtained from cone calorimeter test

Sample	TT1 (s)	p-HRR (kW·m ⁻²)	THR (MJ·m ⁻²)	TSR (m ² ·m ⁻²)	p-COP (g·s ⁻¹)	SEA (m ² ·kg ⁻¹)	av-EHC (MJ·kg ⁻¹)	residual char (%)
PA56	54	1091	117	481	0.007	71	31	0.00
PA56-0.7DDP	51	1009	98	999	0.014	189	26	0.50
PA56-1.2DDP	41	713	95	1218	0.014	197	24	0.97

3.3.2. 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. 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 denser char layer with a smaller microcrystalline structure, which is consistent with the SEM results[34].

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, 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 $\text{R(OH)}_2\text{P=O}$ 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 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 C_{1s} , O_{1s} , and P_{2p} spectra of PA56 and PA56-1.2DDP are depicted in Figure 7 c-e. The C_{1s} 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 O_{1s} 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 P_{2p} 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].

3.3.3. Analysis of the gas phase

The total ion chromatogram of DDP at 350, 400, 450, 500 and 600 °C are shown in Figure 8a, along with the detailed pyrolysis products in Figure 8d. As shown in Figure 8a and d, the main pyrolytic products of DDP are 6-heptenoic acid (d6), o-hydroxybiphenyl (d8), fluorene (d9), 9-methyl-9h-fluorene (d10), 2-(1-phenylethyl) phenol (d11), 1-phenoxy-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 gaseous 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 Figure 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. Besides, methylbenzene (d2/f2) and o-hydroxybiphenyl (d8/f8) generate from DDP and some novel pyrolysis substances (f7, f9, f10, f12) are also found in the chromatogram of PA56-1.2DDP, further revealing that DDP plays a crucial role in the gas phase. In addition, 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 gas, further depressing the combustion degree of PA56.

3.4. 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 Figure 10, FRPA56 releases PO, PO₂ 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.

4. 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. UL-94 V-0 grade is achieved for bio-based PA56 by the incorporation of only 1.0 mol% DDP, which confirms that the DDP copolymerization strategy is effective to improve the 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.

Declarations

Notes

The authors declare no competing financial interest.

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Scheme

Schemes 1 is available in the Supplemental Files section.

Figures

Figure 1

FTIR spectra of PA56 and FRPA56s

Figure 2

^1H -NMR and ^{31}P -NMR spectra of PA56 and FRPA56s

Figure 3

DSC cooling curves (a) and second heating curves (b) of PA56 and FRPA56s

Figure 4

TGA and DTG thermograms of PA56 and FRPA56s in nitrogen (a, b) and air (c, d) atmosphere at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$

Figure 5

Cone calorimetric results of PA56 and FRPA56: (a) HRR, (b)THR, (c) TSR and (d) CO Production Rate

Figure 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

Figure 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

Figure 8

The total ion chromatogram (a-c) and main pyrolysis products (d-e) of DDP, PA56 and PA56-1.2DDP in TGA-GC/MS tests

Figure 9

Main pyrolysis processes of DDP (a) and FRPA56-1.2DDP (b)

Figure 10

Flame-retardant mechanism of FRPA56s in the condensed phase and gas phase

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
- [SupportingInformation.docx](#)