Hybridization of α -zirconium phosphate with hexachlorocyclotriphosphazene and its application in the flame retardant poly(vinyl alcohol) composites

Lingfeng Xu^a, Caihong Lei^{*a}, Ruijie Xu^a, Xiaoqing Zhang^a, Feng Zhang^b

^aGuangdong Provincial Key Laboratory of Functional Soft Condensed Matter, School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, PR China.
Email: Lch528@gdut.edu.cn

^bKingfa Science and Technology Company, Limited, Guangzhou 510520, PR China

ABSTRACT: A planar-like inorganic α -zirconium phosphate (α -ZrP) particles were modified by a kind of cyclophosphazene derivative *via* three-step hybridization method, first modified by melamine (MA), then combined with hexachlorocyclotriphosphazene (HCCP) through nucleophilic substitution and further integrated with excessive MA. Thus, a hybrid flame retardant (HAC) was successfully synthesized. The composites based on poly(vinyl alcohol) (PVA) and HAC were prepared by solution blending. The thermal, mechanical properties and flame retardancy of the composites were studied. It was found that HAC showed a catalytic effect in the initial decomposition stage and promoted the formation of char at high temperatures. When the content of HAC was 15 wt%, the limiting oxygen index (LOI) reached 28.4% and classified V-0 rating, whereas with the same content of fire retardant, for PVA/ α -ZrP and PVA/product of MA with HCCP composites (one kind of intumescent flame retardant IFR), the LOI values were only 24.7% and 27.1%, respectively. The combination of IFR and α -ZrP could remarkably improve the yield and graphitization of char residues, make the char more stable, compact and continuous, inhibiting underlying PVA from contacting heat and oxygen. Moreover, the mechanical properties could be reinforced and toughened with certain content of HAC.

Keywords: hybridization; α -zirconium phosphate; hexachlorocyclotriphosphazene; flame retardancy; synergistic effect; poly(vinyl alcohol).

1. Introduction

In recent years, poly(vinyl alcohol) (PVA) has received particular attention in the field of polymer composites due to its excellent chemical resistance, easy processability, biodegradability, and water solubility [1-5]. In this case, PVA can be widely used in proton exchange membranes, packing materials and artificial biomedical devices, etc. [6-8]. Unfortunately, like other organic thermoplastics, the flammability and poor mechanical properties have limited its application in many fields, and in order to overcome these weaknesses, many researchers have devoted themselves to improving the flame retardancy and mechanical performance of PVA, by preparing PVA composites with layered compounds such as layered silicates, graphite oxide, layered double hydroxides and cationic exchange layered metal phosphates [9-13].

The α -zirconium phosphate (α -Zr(HPO₄)₂•H₂O, α -ZrP) is one of the most important layered nanostructure compounds. Compared with layered silicates, it exhibits some advantages such as higher purity and controllable aspect ratio, more efficient catalyst properties [14-17]. And in many cases, α -ZrP has been exfoliated by organic cationic surfactant such as ethylamine, n-butylamine, Jaffamine M600 and so on [18-20]. However, these modifiers cannot be beneficial to the flame retardancy. Moreover, it has been found that the exfoliated α -ZrP plates will be curled up during the temperature elevated process, which cannot mechanically reinforce the char [21]. It is speculated that the exfoliated α -ZrP is too thin to strengthen the char residues, thus cannot

maintain the efficient flame retardancy at high temperature.

Cyclophosphazene derivative is an important type of inorganic polymeric materials containing alternate phosphorus and nitrogen atoms in the cyclic skeletons. In many kinds of derivatives, hexachlorocyclotriphosphazene (HCCP), a typical inorganic ring, is often used due to the multiple reactive sites on it. The chemically linking cyclotriphosphazene with other IFR (intumescent flame retardant) sources (e.g. acid source, gas source and carbon source) can be considered as a very effective way to achieve a dramatically high efficiency in flame retardancy as well as self-extinguishing property due to the synergism of skeletal phosphorus and nitrogen elements in the phosphazene ring [22,23]. In this case, it can lead to a dramatically high flame-resistance efficiency due to the synergistic effect based on a condensed phase mechanism involving polymer charring and a gaseous phase flame-inhibition mechanism by removing and diluting the combustible materials during fire process [24].

In this present work, some amount of cyclophosphazene derivatives were hybridized on the surface of α -ZrP plates, which could combine the advantages of α -ZrP (like solid acid catalysis effect, lamella barrier mechanism, and also could display as the acid source) with the advantages of cyclophosphazene derivatives (mainly the solid acid sites barriers). Firstly, the inorganic lamellar noncombustible α -ZrP particles were modified by melamine (MA), then combined with hexachlorocyclotriphosphazene (HCCP) through nucleophilic substitution, furthermore, integrated with excessive MA. Thus, a hybrid flame retardant was synthesized successfully. The relationship between macroscopic fire test and microscope morphologies of char residues, along with the chemical components and the graphitization of residual char were investigated by the limiting oxygen index (LOI), vertical burning test (UL-94), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), with the analysis of energy dispersive spectra (EDS), Fourier transform infrared spectroscopy (FTIR) and Laser Raman spectroscopy (LRS). The mechanical properties of PVA composites were investigated as well.

2. Experimental

2.1. Experimental materials

Poly(vinyl alcohol) (PVA, DP 1750 ± 50) was from Fuchen Chemical Reagent Factory (Tianjin, China). Hexachlorocyclotriphosphazene (HCCP, 99%) was purchased from Adamas Reagent, Ltd. and recrystallized twice from petroleum ether before use. Melamine (MA) was purchased from Aldrich Chemical Co. Phosphoric acid (H_3PO_4 , $\geq 85\%$, solution in water, A.C.S. reagent, Sigma-Aldrich) and zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 98%, Aldrich) were used as received. Dimethyl sulfoxide (DMSO), triethylamine (TEA) and absolute alcohol were supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China).

2.2. Preparation of HAC particles

The preparation of HAC particles includes two steps.

First, the lamellar α -ZrP disks were prepared according to the previous studies [25]. In detail, a sample of 10.0 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was mixed with 100 mL 12.0 M H_3PO_4 in a Teflon[®] flask. Then the mixture was sealed into a Teflon[®] pressure condenser at 200 °C for 48 h. The products were washed with deionized water several times and dried in vacuum oven at 70 °C overnight for a constant weight. After that, the dried α -ZrP was ground with a mortar and pestle into fine powders.

In the second step, melamine (0.75 g) and 100 mL DMSO were mixed together in a three-necked flask with stirring and heated to 90 °C, and then, 5.0 g synthesized α -ZrP dispersion

was added gradually with the speed of two drops per second in the flask. After that, the reaction system was keeping refluxing at 90 °C for about 3 h. After α -ZrP was modified by MA, HCCP (2.0 g) and TEA (0.60 g), as the binding acid agent, were introduced into the aforementioned mixture and stirred at reflux temperature for over 10 h. After that, more melamine (1.50 g) was added into upon solution, with the corresponding TEA (1.20 g) was added at same time. Finally, the raw product was filtered and purified with DMSO solvent and deionized water for several times to remove the residual MA and TEA. And then the filtered cake was dried at 80 °C for 24 h in the vacuum oven. The product was ground into a fine powder and used as flame retardant agent HAC. The synthetic procedure of HAC was shown in Fig. 1.

By contrast, the IFR was synthesized as well. Melamine (2.20 g) was mixed in the DMSO solvent with stirring and heated to 90 °C. After MA was totally dissolved, HCCP (2.0 g) and TEA (1.80 g) were added into the mixture and stirred at the same temperature for over 10 h. Finally, the raw product was filtered and purified with DMSO solvent and deionized water for several times to remove the residual MA and TEA. And then the filtered cake was dried at 80 °C for 24 h in the vacuum oven. The product was ground into a fine powder and used as IFR agent.

Fig. 1. Illustration of the synthetic route of HAC.

2.3. Preparation of flame retardant PVA composites

A series of PVA/HAC composites were prepared by solution casting method varying the contents of HAC from 0 to 20 wt%. In a typical procedure, PVA was dissolved in water with vigorous stirring at 85 °C for 2 h, while HAC was dispersed in distilled water to form suspension and sonicated for 30 min. After that, the suspension was gradually introduced into the PVA solution and mixed at 90 °C for further 2 h. For uniform dispersion of HAC in PVA, both stirring and ultra-sonicating were necessary during the process of suspension. Then the translucent

solution was coated onto glass plates by a rod with certain interval, and dried in an oven at 40 °C for 2 days. After that, the so-formed films were peeled off from the plates and further heated at 70 °C for 6 h to remove residual water. The 0.5 mm thick films were obtained and used for relevant tests, as shown in Table 1. For comparison, the composites of PVA/ α -ZrP and PVA/IFR with 15 wt% of α -ZrP and IFR, respectively, were also prepared.

Table 1

Formulations of PVA and PVA/HAC solution.

Sample	PVA (wt%)	HAC (wt%)	α -ZrP (wt%)	IFR (wt%)
PVA	100	0	0	0
PVA/ α -ZrP	85	0	15	0
PVA/IFR	85	0	0	15
PVA/ α -ZrP/IFR	85	0	12.6	2.4
PVA/HAC1	95	5	0	0
PVA/HAC2	90	10	0	0
PVA/HAC3	85	15	0	0
PVA/HAC4	80	20	0	0

2.4 Characterization

The Fourier transform infrared (FT-IR) spectra were investigated by a Nicolet 6700 FTIR instrument at room temperature. The samples were mixed with KBr pellets and scanned 32 times over spectral range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1} .

The field-emission scanning electronic microscopy (FESEM) observed on SU8010 (Hitachi, Japan) was used to investigate the morphology of HAC particles and the surface of char residue of the flame-retardant PVA composites after the vertical burning test was investigated by S3400N (Hitachi, Japan). The surface of the particles and the char residue were sputter-coated with a conductive gold layer before observation. EDS result of the residual char was measured by an energy dispersive X-ray spectrometer.

The thermogravimetric analysis (TGA) was characterized by a TG SDT Q600 (TA Instruments, U.S.) thermogravimetric analyzer at temperatures ranging from room temperature to 600 °C, and with a linear heating rate of 10 °C/min under air atmospheres. The weight of each sample was kept 3-5 mg and the same operation was used for each sample.

Limiting oxygen indexes (LOI) were measured by a LOI analyzer (JF-3, Jiangning Co. Ltd., Nanjing, China) with sheet dimensions of 140×52×0.5 mm^3 according to GB/T 2406-93 standard. The vertical burning test of each sample was evaluated on a CZF-5-type instrument (ShineRay Instrument Co. Ltd., Nanjing, China) with sheet dimensions of 130×13×0.5 mm^3 according to ASTM D3801. An average of at least five replicas were used for each sample.

To study the catalytic carbonization behavior of HAC in PVA matrix, the graphitization degrees of the chars were carried out at room temperature with a Lab RAM Aramis Micro-Raman spectroscope (Horiba, France) with excitation by 632.8 nm laser line scanning in the range of 500-2000 cm^{-1} .

The tensile tests were carried out on a DXLL-5000 electronic universal mechanical testing machine (Shanghai D&G Measure Instrument Co., Ltd). The samples were cut into strips

according to GB/T 1039-92 and tested at room temperature with a gauge length of 20 mm and crosshead speed of 20 mm/min. And the values were averaged over five measurements.

3. Results and discussion

3.1 Characterization of HAC

3.1.1 Field-emission scanning electron microscopy analysis

The morphologies of the prepared HAC particles were studied by FESEM. As shown in Fig. 2a, the α -ZrP particles with angular shape show lamellar structure, and the smooth and clear surface of α -ZrP can be seen as well. And in Fig. 2b, it can be seen that the surface color of HAC is lighter than α -ZrP, proving that obviously modified structure exists. On the other hand, some fine particles accumulating on the surface of α -ZrP can be observed, which may be attributed to the combination product of MA with HCCP through nucleophilic substitution, defined as IFR modifiers in this paper. In this case, the surface of HAC has become rougher. Some cracked structures have been observed on the edges of α -ZrP disks, and some IFR modifiers gather here. A hybrid flame retardant combining α -ZrP with a kind of IFR modifier is successfully prepared.

Fig. 2. FESEM images of raw α -ZrP (a) and HAC particles (b).

3.1.2 FT-IR analysis

The chemical structure of α -ZrP and HAC was further characterized by FT-TR, and the spectra of α -ZrP and HAC are shown in Fig. 3. The characteristic peak at 1250 cm^{-1} is attributed to the stretching vibration of P-O-H, whereas the characteristic absorption of 3593 cm^{-1} and 3510 cm^{-1} are related with the asymmetric stretching vibration of O-H inside the layer of α -ZrP [27]. By comparing the FTIR of α -ZrP and HAC, it can be found that the characteristic absorption of 3301 cm^{-1} is owing to the stretching vibration bands of N-H, which comes from MA. The new intensive absorption at 1662 cm^{-1} and 1505 cm^{-1} are attributed to the bending vibration of C=N skeleton, further confirming the existence of MA [28]. Moreover, the characteristic peaks at 856 cm^{-1} and 780 cm^{-1} are corresponding to the P-N stretching vibration and H-C-N bending, respectively, while the absorption bands of C-N stretching vibration at 1049 cm^{-1} shows a considerable increase in the absorbance intensity [29]. The obvious peak at 1182 cm^{-1} is owing to the P-N-C bending, which indicates that MA has been combined with HCCP.

Fig. 3. FT-IR spectra of α -ZrP and HAC particles.

3.1.3 TGA of α -ZrP and HAC particles

Fig. 4 gives the TGA curves of α -ZrP, HAC and MA-HCCP (IFR modifier), and the thermal decomposition of these particles mainly takes place in three weight loss step. For α -ZrP, the mass is the lowest, 9.81%. It undergoes a dehydration process with the broad weight loss temperature range from 100-400 °C, which may be assigned to the volatilization of absorbed water and crystal water inside the α -ZrP plates. Then a condensation reaction of the monohydrogen phosphate (P-OH) to zirconium pyrophosphate (ZrP_2O_7) at about 585 °C follows. The process can be illustrated as follows [30]:

As for MA-HCCP, the mass loss is the highest, 90.1%, which is mainly attributed to the oxidation of MA-HCCP producing NH_3 , CO , CO_2 , etc. For comparison, the weight loss of HAC is 20.9 %, which starts early at the lower temperature range, which should be attributed to the escape of absorbed water and interlayer water of HAC, the mainly oxidation of IFR on the outer surface of α -ZrP. In the next step, the residual IFR is further degraded, with the damaged plates caused by the condensation of monohydrogen phosphate. Moreover, the content of IFR in HAC composite can be calculated according to the above TGA results, which is about 15.7 wt%.

Fig. 4. TGA curves of α -ZrP, HAC and MA-HCCP (IFR) under air atmosphere.

3.2 Thermogravimetric analysis of PVA/HAC composites

The thermal stability was studied by TGA under air atmosphere. Fig. 5 gives TG and differential thermogravimetric (DTG) curves. The data are listed in Table 2. It can be seen that the decomposition of PVA occurs mainly in two steps. The first mass loss around 279 °C is attributed to the elimination of water and residual acetate groups, since PVA is a kind of polyhydroxy polymer with a large amount of acetate group remained in its molecular chains. The second decomposition step is around 418 °C, which can be assumed to be cyclization reaction accompanying with the scission of PVA chains. Compared with pure PVA, it can be observed that with more addition of HAC flame retardants, the initial decomposition temperature (T_{initial}) of PVA/HAC composites is decreased by 9.04-27.11°C. This means that HAC can catalyze the decomposition of PVA chain due to the existing solid acid sites on the surface of HAC [31]. Furthermore, the first maximum-rate temperature (T_{max1}) is decreased in different degrees with more amount of HAC additives. Combined with the TGA results of HAC, it is suggested that with more HAC decomposed, more acid solid sites are exposed to the PVA chains and the catalytic degradation becomes more serious [32]. However, the thermal stability of the second step is enhanced. The second maximum-rate temperature (T_{max2}) of composites are increased by 2.39-25.18 °C. Meanwhile, the char yield of composites (5.11 wt%-22.12 wt%) are remarkably improved in comparison with neat PVA (1.02 wt%).

In the DTG curves, the peak height represents the rate of mass loss. The mass loss rates of composites in the first and second step are higher than those of neat PVA, probably since the decomposition derivatives of HAC can catalyze the formation of the carbonaceous char, and this effect takes place during the whole process of degradation. Moreover, with more content of HAC, the peak height is decreased, meaning that HAC can significantly reduce the heat release rate when its content reaches a high level.

In order to further evaluate the synergistic effect between the IFR modifier and α -ZrP plates, the theoretical calculated data based on the follow formula and the experimental data of final char residue mass are shown in Table 3.

$$W_{\text{cal.}}(\text{Com}) = x \times W_{\text{exp.}}(\text{PVA}) + y \times W_{\text{exp.}}(\text{HAC}), x+y=1$$

$W_{\text{exp.}}(\text{PVA})$: Value of weight given by the experimental char residue of neat PVA;

$W_{\text{exp.}}(\text{HAC})$: Value of weight given by the experimental char residue of HAC;

$W_{\text{cal.}}(\text{Com})$: Theoretical char residue mass computed by linear combination of $W_{\text{exp.}}(\text{PVA})$ and $W_{\text{exp.}}(\text{HAC})$;

x, y: the weight percent of the PVA and HAC in composite, respectively.

From the results listed in Table 3, it can be seen that when the content of HAC is higher than 5 wt%, the char residue masses given by experiment are higher than theoretical computed values, meaning that HAC can promote the char formation and improve the yield of the char residue. There may exist a synergism effect between the α -ZrP plates and IFRs combined with it, and it is beneficial to improve the thermal stability and flame retardancy performance of PVA composites [33,34].

Fig. 5. TGA and DTG curves of PVA composites.

Table 2

TG and DTG data in air atmosphere.

Sample	T_{initial}^a (°C)	T_{max1}^b (°C)	T_{max2}^c (°C)	Residue ^d (wt%)
PVA	251.64	279.80	418.70	1.02
PVA/HAC1	242.60	265.89	443.88	5.11
PVA/HAC2	236.51	253.70	436.90	11.03
PVA/HAC3	228.24	245.93	430.90	16.14
PVA/HAC4	224.53	240.58	421.09	22.12

^a T_{initial} is the initial degradation temperature (temperature at 5% weight loss). ^b T_{max1} is the first maximum-rate degradation temperature. ^c T_{max2} is the second maximum-rate degradation temperature. ^dResidue is the weight of char residue at 600 °C.

Table 3

Theoretical data and experimental data of char residue mass.

Sample	$W_{\text{cal.}}(\text{Com})$ (wt%)	$W_{\text{Exp.}}(\text{Com})^a$ (wt%)
PVA/HAC1	5.23	5.11
PVA/HAC2	9.46	11.03
PVA/HAC3	13.70	16.14
PVA/HAC4	17.90	22.12

^a $W_{\text{Exp.}}(\text{Com})$ is the weight of char residue given by the experiment.

3.4 Effect of HAC on the flame retardancy properties of PVA composites

Table 4 gives the limiting oxygen index (LOI) values and vertical burning test (UL-94) results of pure PVA and PVA systems with different additives. Pure PVA is highly combustible. Its LOI value is only 19.5 % and it is classified as no rating (NR) during the vertical burning (UL-94) test. The presence of 5 wt% HAC enhances the LOI value to 22.2 %, although it cannot pass the UL-94 test due to the serious dripping. However, with more content of HAC additives, the LOI values of PVA composites are remarkably increased and higher UL-94 ratings are obtained. When the addition amount of HAC reaches 10 wt%, the LOI value of PVA/HAC2 ascends to 25.7% and reaches the UL-94 V-2 rating. Especially, the LOI values of PVA/HAC3 and PVA/HAC4 are increased to 28.1% and 30.7%, respectively, while the two composites have reached the UL-94 V-0 rating without dripping. Compared to the sample PVA/HAC3, with the same amount of fire retardants, the LOI values of PVA/ α -ZrP and PVA/IFR are only 24.7% and 27.1%, respectively. The flame retardancy cannot satisfy V-0 request. Moreover, when the α -ZrP is mixed directly with

IFR in the same amount of each component as that in sample PVA/HAC3, the LOI is only 25.8%. Obviously, the flame retardant performance is worse than that of PVA/HAC3, which indicates that it is necessary to cover the solid acid sites of α -ZrP to protect the PVA from early degradation. And furthermore, hybridization of IFR with α -ZrP plates can be beneficial for the dispersion of IFR, in the meantime, to make HAC well dispersed in the matrix, which will be conducive to flame retardancy to some extent.

Table 4

Flame retardancy of the PVA composites blended with different content of HAC.

Sample	LOI (%)	UL-94	Dripping or not
PVA	19.5	NR	Yes
PVA/ α -ZrP	24.7	NR	Yes
PVA/IFR	27.1	V-1	No
PVA/ α -ZrP/IFR	25.8	V-2	Yes
PVA/HAC1	22.2	NR	Yes
PVA/HAC2	25.9	V-2	Yes
PVA/HAC3	28.4	V-0	No
PVA/HAC4	30.7	V-0	No

3.5 Char Residue Analysis

3.5.1 Morphology investigations and EDS analysis of char residue

In order to study the flame retardancy mechanism, the morphologies of the char residues collected after the LOI tests were investigated by SEM, as shown in Fig. 6. It can be found that when sample PVA/ α -ZrP is burned out, the outer surface of its char residues seems fluffy and puffy, and large amount of pores are observed on the inner surface of PVA char (as shown in Fig. 6a-b), which indicates that simple α -ZrP cannot perform better flame retardancy. And from the Fig. 6c-d, it can be seen that the swollen inner structure with expanded outer surface occurs, and is extremely messy and seems to have been crushed. This phenomenon demonstrates that char is not stable owing to the cracks on the outer surface. For PVA/HAC3 (as shown in Fig. 6e-f), the thick, compact, continuous char layers without pores appear on both sides of residual chars, which could provide a good barrier to the inhibition of heat, mass and flammable pyrolysis gases transferring between the flame zone and the substrate during fire test, thus protecting the underlying materials from further burning and pyrolysis [35,36]. This morphology may be caused by the synergistic effect between IFR modifiers and α -ZrP plates, the former affording a solid acid sites barriers and volatilized in the early degradation stage, and the latter catalyzing the cross-linking of PVA chains during combustion, and furthermore, strengthening the char barriers to make it more intact and robust to display planar inhibition function, thus to improve the flame retardancy at higher temperature.

To further understand the quality of the residual char, the micromorphology and composition of the char layer were also observed by the scanning electron microscopy-energy dispersive X-ray spectrometry (SEM-EDS), and the results were presented in Fig. 7. It is found that the outer surface and inner char surface of PVA/HAC have the same elements but with different relative content of C, O, P and Zr. It can be detected that more content of carbon elements is presenting on the outer surface, while more content of other elements is existing on the inner surface. In this case, it can be summarized that more HAC char is accumulating on the interior surface, and more

PVA char is gathering on the outer surface, which may be due to the different densities of substance and with different transferring velocities, thus form a gradient distribution inside the char. This structure may be mechanically strengthened by the closer lamellar adjacent layers (see discussion in 3.2) and be helpful to form a thermostable char, with the promotion of cross-link network during the combustion processes. As a result, the flame retardancy is improved indeed by the combination of physical morphologies advantages and chemical catalyst advantages together.

Fig. 6. Morphologies of char obtained from the samples after LOI test: outer surface of PVA/ α -ZrP (a), PVA/IFR (c), PVA/HAC3 (e); inner surface of PVA/ α -ZrP (b), PVA/IFR (d), PVA/HAC3 (f).

Fig. 7. EDS results of outer and inner surface: (a) outer surface of PVA/HAC3, (b) inner surface of PVA/HAC3.

3.5.2 FTIR spectra of char residues

In order to analyze how HAC influences the degradation process, FTIR spectroscopy was used to analyze the charred layer composition of PVA/HAC4. The chars were collected after burning in a muffle furnace at 400, 500, 600 and 700 °C for 5 min. From Fig. 8b-d, first of all, there are no obviously IFR characteristic peaks, meaning that IFR has been almost decomposed and volatilized before 500 °C. Then, it can be found that the peak at 987 cm^{-1} can be ascribed to the stretching vibration of P-O-P [4]. The characteristic absorption peaks ($\sim 1200 \text{ cm}^{-1}$ and $\sim 1150 \text{ cm}^{-1}$) in the 1100-1300 cm^{-1} range are assigned to the P-O bands belonging to the HAC char, ZrP_2O_7 . The results confirm that $\text{Zr}(\text{HPO}_4)_2$ is further degraded with the temperature around 500 °C, and the lamellar structure is destroyed, induced by the dehydration of P-OH [37]. Besides that, the peak at 1043 cm^{-1} is probably owing to the P-O-C stretching vibration [38]. Possible condensation reaction between HAC and PVA chain cracks occurs. At last, sharp absorption peaks at 1630 cm^{-1} and 1386 cm^{-1} are attributed to C=C stretching vibration of the aromatic compounds and kept its relative intensities in all spectra, mean more carbon char residues are produced [39]. Based on these results, it can be concluded that incorporation of HAC could release IFR in the primary degradation of PVA composites, and it could catalyze the conversion of PVA into unorgano-phosphorus compounds cross-linked with aromatic structure during combustion. The char layers are mainly consisted of graphite-like complexes, with aromatic structures bridged by P-O-C and P-O-P bonds [40].

Fig. 8. FTIR spectra of residues from PVA/HAC4 treated for 5 min at (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C.

3.5.3 Raman analysis

Raman spectra are usually used to characterize graphitic structure of materials, and to evaluate the order degree of carbon materials, in terms of two characteristic bands: the D-band ($\sim 1350 \text{ cm}^{-1}$, which is associated with the vibration of carbon atoms with dangling bonds in the plane terminations of disordered graphite) and the G-band ($\sim 1580 \text{ cm}^{-1}$, which corresponded to an E_{2g} mode of hexagonal graphite and was related to the vibration of sp^2 -bonded carbon atoms in graphite layers, showing the graphitic structure) [41]. Fig. 9 presents the Raman spectra of the char residue for different samples after UL-94 test. The graphitization degree of the char can be calculated by ratio of integrated intensity of the D and G bands ($R = I_D/I_G$). The low R-value corresponds to high graphitization degree [42]. When uncovered α -ZrP is mixed with PVA, the R-value is 1.21, whereas with the same addition of IFR, the R-value is decreased to 1.08, indicating a more graphitic structure is formed. And when blended with same amount of HAC

particles, the R-value is further decreased to 0.73, which demonstrates that higher graphitization degree char is obtained when α -ZrP is combined with IFR modifiers. Therefore, one could conclude that HAC could transfer amorphous char into graphitic structure efficiently, thus, the strength of char layer is enhanced and become more compact and stable, performing a better barrier effect during combustion. Meanwhile, it can be considered that aromatic compounds are the graphitic carbon char, mainly, combined with the results that shown in the above FT-IR spectra.

Fig. 9. Raman spectra of the char residues after UL-94 testing of (a) PVA/ α -ZrP, (b) PVA/IFR, (c) PVA/HAC3.

3.6 Flame retardancy mechanisms of PVA/HAC composites

HAC is efficient to improve the flame retardancy of PVA, and based on the above results, it can be deduced that there is a comprehensive flame-retardant mechanism, including the gas phase mechanism and condensed phase mechanism, the synergism between IFR and α -ZrP plates. The main degradation process can be separated into three stages, and intermediate products in each stages are shown in Fig. 10 (I represents the first degradation stage, II represents the second degradation stage, and III represents the third degradation stage). In the first degradation stage, the IFR is decomposed into MA and phosphazene ring-opened compound, also with the α -ZrP plates produced (chemical reaction 1.1). And with the temperature rising, the elimination reaction of PVA chain has taken place during the first stage (chemical reaction 1.2). In this case, MA could act as the gas source to dilute the combustible pyrolysis gases, and the phosphazene ring-opened compound would further decompose into ammonia (gas source) and metaphosphoric acid (acid source). Moreover, the phosphazene ring-opened compound is easily generated to phosphorus-based radicals ($\text{PO}\cdot$, $\text{PO}_2\cdot$, etc.) which could display as the radical scavengers to trap the $\text{H}\cdot$ and $\text{HO}\cdot$ for combustion reactions in the gas zone, thus be beneficial to flame retardancy.

Besides that, the acid solid sites are exposed to PVA chain due to the degradation of IFR in this stage, which could act as the acid source as well. Then in the second degradation, the metaphosphoric acid could accelerate the dehydration of PVA, with the catalysis effect of Lewis acid sites uncovered on the surface of α -ZrP plates, and the Diels-Alder reaction would happen among the ethylene oligomer (chemical reaction 1.3) [21]. In the last stage, the polymers are converted into an intermediate product of aromatic structure by intramolecular cyclization reactions. Besides that, it is assumed that the solid acid can catalyze the carbonization of PVA and in that case, catalyze the cyclodehydrogenation reaction to transform substituted aromatic into polycyclic aromatic hydrocarbons. Thus, the graphitic carbon is constituted by stacking the polycyclic aromatic species. According to the carbon structure, the carbonaceous char residues consists of amorphous carbon and crystalline carbon char or graphitic char. And the formation of graphitic structure char during the combustion can further improve the flame retardancy of composites by reducing the releasing of flammable pyrolysis cracks. As discussed above, the incorporation of HAC could not only dilute the flammable gaseous molecules in the gas phase and act in the vapor phase by a radical mechanism to interrupt the combustion of PVA, but also could facilitate the transformation of the poorly graphitizable carbon to a relatively more crystalline char in the condensed phase, thus increasing the degree of graphitization of char residues. Besides that, it could act as adhesive to cross-link the polyaromatic structure to make char intact and robust, which leads to an improvement of the char quality. Moreover, with the incorporation of IFR and α -ZrP plates, the above reactions are accelerated and the synergism effect is presented.

Fig. 10. Schematic illustration of the flame retardant mechanism of PVA/HAC composites.

3.7 Mechanical properties of PVA/HAC composites

In the end, the mechanical properties of PVA samples were investigated, and the results are presented in Table 5. It can be seen that the addition of HAC could enhance the tensile strength and the elongation at break when the content is below 10 wt%. The PVA composites could not

only be reinforced but also be toughened by HAC. However, both the tensile strength and the elongation at break are significantly decreased when the addition of HAC exceeds 10 wt%. The reason may be the possible aggregation of HAC in the matrix.

To illustrate the results of macroscopic mechanical tests, the morphologies of brittle fracture surface of PVA composites were further investigated by SEM (as shown in Fig. 11). It can be observed that the samples with more HAC flame retardants exhibit some kind of obvious ‘cavities’, as marked in the red circles in the images. Furthermore, it can be seen that the ‘cavities’ occur around the aggregation of HAC, suggesting that HAC has become the defects and weaken the interfacial interaction between the phases [43]. In this case, it can be concluded that the continued increase of HAC amount makes flame retardancy better but reduces the mechanical properties to some extent.

Table 5

Tensile properties of PVA and its composites.

Sample	Tensile strength (MPa)	Elongation at break (%)
PVA	45.1 ± 1.0	219.8 ± 4.8
PVA/HAC1	51.5 ± 1.4	231.5 ± 3.1
PVA/HAC2	58.2 ± 1.2	267.2 ± 2.7
PVA/HAC3	47.3 ± 1.1	241.4 ± 3.6
PVA/HAC4	34.8 ± 0.9	200.3 ± 1.2

Fig. 11. SEM micrographs of brittle fracture surface of (a) PVA, (b) PVA/HAC1, (c) PVA/HAC2, (d) PVA/HAC3 and (e) PVA/HAC4 composites.

4. Conclusions

A planar-like structure of α -ZrP was pre-intercalated by a gas source, MA, and further modified by a kind of cyclophosphazene derivative, HCCP. A hybrid flame retardant HAC was synthesized and mixed with PVA via solution blending. HAC showed a catalytic effect in the initial decomposition stage and promoted the formation of char at high temperatures. When the addition of HAC was increased to 15 wt%, the composites could reach a LOI value of 28.4% and classified V-0 rating. The main function of IFR modifiers here acted as solid acid site barriers, to protect PVA from early degradation, and could display synergistic effect with α -ZrP plates to some extent. The HAC residues can act as the skeleton of the char residues, and also to improve the graphitization of char residues, strengthening the char and improving its thermal stability. However, high content of HAC (exceeded 10 wt%) would decrease the tensile strength and elongation at break. All results indicated that HAC showed a significant effect on the flame retardancy for PVA system, but its content should be controlled in a certain range.

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Table 1
Formulations of PVA and PVA/HAC solution.

Sample	PVA (wt%)	HAC (wt%)	α -ZrP (wt%)	IFR (wt%)
PVA	100	0	0	0
PVA/ α -ZrP	85	0	15	0
PVA/IFR	85	0	0	15
PVA/ α -ZrP/IFR	85	0	12.6	2.4
PVA/HAC1	95	5	0	0
PVA/HAC2	90	10	0	0
PVA/HAC3	85	15	0	0
PVA/HAC4	80	20	0	0

Table 2
TG and DTG data in air atmosphere.

Sample	T _{initial} ^a (°C)	T _{max1} ^b (°C)	T _{max2} ^c (°C)	Residue ^d (wt%)
PVA	251.64	279.80	418.70	1.02
PVA/HAC1	242.60	265.89	443.88	5.11
PVA/HAC2	236.51	253.70	436.90	11.03
PVA/HAC3	228.24	245.93	430.90	16.14
PVA/HAC4	224.53	240.58	421.09	22.12

^aT_{initial} is the initial degradation temperature (temperature at 5% weight loss). ^bT_{max1} is the first maximum-rate degradation temperature. ^bT_{max2} is the second maximum-rate degradation temperature. ^dResidue is the weight of char residue at 600 °C.

Table 3
Theoretical data and experimental data of char residue mass.

Sample	W _{cal.} (Com) (wt%)	W _{Exp.} (Com) ^a (wt%)
PVA/HAC1	5.23	5.11
PVA/HAC2	9.46	11.03
PVA/HAC3	13.70	16.14
PVA/HAC4	17.90	22.12

^aW_{Exp.}(Com) is the weight of char residue given by the experiment.

Table 4
Flame retardancy of the PVA composites blended with different content of HAC.

Sample	LOI (%)	UL-94	Dripping or not
PVA	19.5	NR	Yes
PVA/ α -ZrP	24.7	NR	Yes
PVA/IFR	27.1	V-1	No
PVA/ α -ZrP/IFR	25.8	V-2	Yes
PVA/HAC1	22.2	NR	Yes
PVA/HAC2	25.9	V-2	Yes
PVA/HAC3	28.4	V-0	No
PVA/HAC4	30.7	V-0	No

Table 5
Tensile properties of PVA and its composites.

Sample	Tensile strength (MPa)	Elongation at break (%)
PVA	45.1±1.0	219.8±4.8
PVA/HAC1	51.5±1.4	231.5±3.1
PVA/HAC2	58.2±1.2	267.2±2.7
PVA/HAC3	47.3±1.1	241.4±3.6
PVA/HAC4	34.8±0.9	200.3±1.2

Figure1

Figure2

Figure3

Figure4

Figure5

Figure6

Figure7

Figure8

Figure9

Figure10

Figure11