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焦磷酸三聚氰胺与聚乙烯醇分子之间的氢键相互作用提高聚乙烯醇水凝胶薄膜的阻燃性能

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摘　要：文章通过聚乙烯醇(PVA)与硼酸(H3BO3)交联制备成水凝胶薄膜,添加焦磷酸三聚氰胺(MPP)提高PVA/MPP 复合水凝胶薄膜的阻燃性能,当添加 20 wt% MPP 时,PVA 阻燃性能达到 UL-94 V-0 级,MPP 的加入可有效降低水凝胶薄膜的热释放速度(HRR)和发烟量。实验结果表明,MPP 与 PVA 分子之间的氢键相互作用可以保持材料的力学性能,提高材料的阻燃性能。PVA/MPP 水凝胶膜的阻燃机理是气相与凝聚相阻燃机理的协同作用,MPP 分解为三聚氰胺和磷酸,然后三聚氰胺转化为 N_2 和 CO_2,磷酸促进 PVA 水凝胶形成连续致密的炭层,阻碍了与外界的氧气和热量交换。

关键词：聚乙烯醇；焦磷酸三聚氰胺；凝胶；氢键；阻燃
中图分类号：TQ314.24　　**文献标志码**：A

Flame retardant effect of melamine polyphosphate on Polyvinyl alcohol hydrogel film

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Abstract: In this work, Polyvinyl alcohol (PVA) was cross-linked via Boric acid(H_3BO_3) and prepared to be the hydrogel film. MPP is used to improve the flame retardant properties of the PVA hydrogel films. The experimental results showed that the PVA /MPP hydrogel films could achieve UL-94 V-0 rating with a 20 wt% addition of MPP which could effectively reduce the HRR and the smoke emission of the PVA hydrogel films. The flame retardant mechanism of the PVA/MPP hydrogel films is a synergistic effect of gas-phase with condensed-phase flame retardant mechanism. MPP decomposed into melamine and phosphoric acid, then melamine converted to N_2 and CO_2; Phosphoric acid promoted the PVA hydrogels formation of a continuous and dense char layer which hinders the exchange of oxygen and heat with the outside. At the same time, because of the interaction between MPP and PVA, the mechanical properties of PVA are maintained while the flame retardancy of PVA is improved.

Key words: polyvinyl alcohol; melamine polyphosphate; hydrogel; hydrogen bond; flame retardant

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1 Introduction

Polyvinyl alcohol (PVA) is a low-cost water-soluble polymer with excellent hydrophilicity, biocompatibility, biodegradability and processability. It is widely used in many fields, such as textile, construction, and coating[1].

PVA can be prepared as a hydrogel containing water by chemical cross-linking (e. g. covalent bonds) and physical cross-linking (e. g. ionic bonds, hydrogen bonds, electrostatic interactions, van der Waals forces)[2]. However, PVA is highly flammable with a 19% limiting oxygen index due to its structure composed of carbon, hydrogen, and oxygen atoms[3]. And so flame retardancy is often required for many PVA products, such as PVA films used in packaging, electronic appliances, and lithium-ion battery separators. Therefore, improving the flame retardant performance of PVA products has attracted more and more attention from researchers in the fire science community.

To improve the flame retardant properties of PVA, two kinds of flame retardant methods are employed, one is adding halogen-free flame retardants, including the chemicals containing phosphorus/nitrogen (P/N), silicon (Si), and boron (B)[4]. Such additive flame retardants, with large amount of addition, often lead to a decrease of the mechanical properties[5]. The other is using the interaction between PVA and flame retardants to improve the flame retardant of PVA composites through grafting, cross-linking[6] and hydrogen bonding[7]. Liu, et al.[8] firstly prepared flame retardant PVA film by blending the flame retardant agent 9, 10-dihydro9-oxa-10-phosphoheterophen-10-oxide-γ-(2, 3-epoxypropoxypropyl) propyl trimethoxysilane (DPP) with PVA, DPP was grafted onto the surface of PVA film through chemical bonds while heating. A PVA hydrogel containing metal ions was prepared by cross-linking acrylic acid containing metal ions with PVA. The experimental results stated that the addition of metallic calcium ions increased the LOI value and improved the flame retardancy of PVA, the formation of carbon layers containing calcium carbonate prevented the entry of oxygen and the volatilization of volatiles[9]. Wang's group[10] prepared PVA/guanidine phosphate (GP) films with high transparency, based on the interaction of their intermolecular hydrogen bonds between PVA and GP. The GP flame retardant PVA membrane with high transparence had tensile strength increased by 47% and its flame retardant achieved a UL94 V-0 rating when the content of GP is 15 wt%. It suggested that the interaction between GP and PVA effectively promoted formation of a continuous and stable char in the condensed phase.

Melamine Polyphosphate (MPP) is a typical halogen-free flame retardant containing nitrogen and phosphorus components[11], its flameretardant mechanisms involve gaseous phase (by nitrogen component) and condensed phase (by phosphorus component), accordingly possessing remarkable N-P synergistic effects. Amino group ($-NH_2$) is rich in its molecule structure, which easily forms hydrogen bonds with hydroxyl group($-OH$) of PVA[12].

In this work, PVA is cross-linked with H_3BO_3 and formed PVA hydrogel film[13]. With the flame retardant MPP, the flame retardant properties of PVA is improved without almost no reduction of the mechanical properties of PVA. The flame retardant properties and mechanism of PVA/MPP hydrogel films are tested by vertical burning, conical calorimeter and PY-GC-MS, so as to obtain a new flame retardant material data. At the same time, the interaction between MPP and PVA in the PVA hydrogel films is investigated.

2 Experiment

2.1 Materials

(PVA-1799) was supplied by Kelong Chemical Reagent Corporation (Chengdu, China). Melamine ($C_3H_6N_6$), Boric acid (H_3BO_3) and Phosphoric acid (H_3PO_4) were supplied by Xilong Science Co. Ltd. (Shantou, China). All the chemicals were of reagent grade and were utilized as received without further purification unless otherwise specified.

2.2 Preparation of MPP and PVA/MPP composite hydrogels

2.2.1 Synthesis of MPP

MPP is generally prepared by the following method[14]: 100 g of melamine was added into 400 mL water in a three-necked flask, stirred mechanically and dispersed, then 160 g of phosphoric acid (85% concentration) was added by drop while stirring, after about 30 minutes, heated to 90 ℃, reacted for 2 h, cooled, filtered, dried (120 ℃), and finally calcined at 300 ℃ for 3 h in a muffle furnace. The synthetic route is shown in Fig. 1[15]:

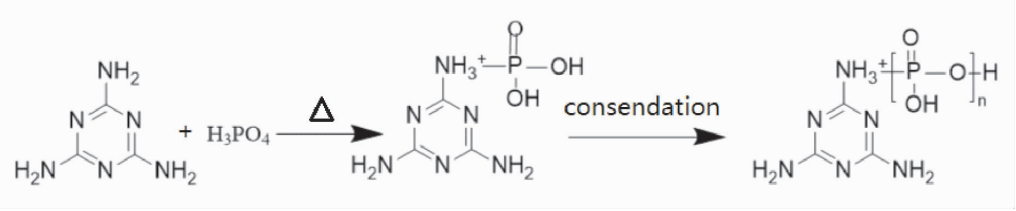


Fig. 1　The synthetic route of MPP

2.2.2 Preparation of the PVA/MPP hydrogel films

(1) 8 g of PVA powder and 92 g of distilled water were added to a round-bottomed three-mouth flask, first swelled for 1 h, and then mechanically stirred for 2 h at 95 ℃, cooled at room temperature, to obtain 8 wt% of PVA aqueous solution.

(2) According to the formulation in Table 1, MPP was added to PVA solution, stirring evenly, then a certain amount of H_3BO_3 was used as cross-linking agent and added to the above solution, stirred quickly, casting into the mould for cross-linking to obtain a PVA/MPP hydrogels, then dried at room temperature to form a film. The films were prepared by solution casting method and their preparation process is shown in Fig. 2.

Table 1　Formulation of PVA/MPP composite hydrogels　g

Samples	PVA(8 wt%)	MPP	H_3BO_3
PVA1	100	0	0.8
PVA2	100	10	0.8
PVA3	100	20	0.8
PVA4	100	30	0.8

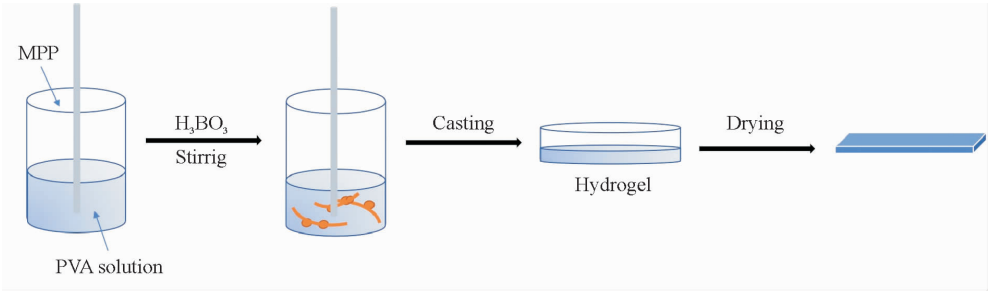


Fig. 2　Preparation of MPP flame retardant PVA hydrogel films

2.3 Characterization

The Fourier-transform infrared spectroscopy (FT-IR) spectra was performed using a Nicolet 6 700 spectrometer in the frequency region of 500 ~ 4 000 cm^{-1} with a resolution of 4 cm^{-1} to detect the functional groups on MPP, PVA and PVA/MPP.

The surface morphology of charring layer is characterized by a scanning electron microscope (SEM) (JSM-5900LV, JEOLLtd, Tokyo, Japan) with a conductive gold coating at an accelerating voltage of 10 kV. Energy dispersive spectrometry (EDS) (INCA, Oxford Instrument) is carried out to analyze the surface elemental compositions.

The thermogravimetric analysis (TGA) was performed on a TA Instrument (TGA Q50) from 50 ℃ to 700 ℃ at a heating rate of 10 ℃ · min^{-1}. The samples (about 5 mg) were analyzed under a nitrogen atmosphere.

The vertical burning test was measured by a vertical burning instrument (CZF-3, Jiangning). The

samples (300 mm × 89 mm) were tested according to GB/T 5455—2014.

The cone calorimeter test was performed on a Cone Calorimeter (FTT007, Fire Testing Technology Ltd., UK) according to ISO5660 standard. The specimens (100 mm × 100 mm × 2 mm) were wrapped in aluminum foil and exposed to a heat flux of 35 kW · m^{-2}.

The pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) was employed to study the pyrolysis gaseous products of the PVA/MPP composite hydrogels, testing conditions: Helium was used as a carrier gas at speed: 15 mL · min^{-1}; injector temperature: 250 ℃; pyrolysis temperature: 600 ℃; mass scanning range: 10 ~ 600 Da; ionic detector: 250 ℃; quantity of the control sample: 2.094 g; quantity of flame-retardant sample: 2.369 g. The column was kept at 50 ℃ for 5 min, and heated up to 230 ℃ at a rate of 10 ℃ · min^{-1}, and then maintained at 230 ℃ for another 5 min.

The mechanical properties of all samples were tested on a universal tensile testing machine according to GB/T 3923.1—2013 with a tensile speed of 20 mm · min^{-1}.

The rheological behavior of PVA-based hydrogels in an oscillating shear field was studied using an Anton Paar Physica shear rheometer (MCR 300) equipped with parallel plate geometry (diameter = 25 mm). The frequency sweep experiments in the range of 0.1 ~ 100 rad · s^{-1} were performed under an air atmosphere, at ambient temperature, and with a strain amplitude of 0.1%.

3 Results and Discussion

3.1 Characterization of MPP

3.1.1 FTIR analysis

In the infrared spectra of Fig. 3 for MPP, the peaks at 3 000 ~ 3 500 cm^{-1} are characteristic peaks of $-NH_2$, the peaks at 1 661.78 cm^{-1} and 1 469.31 cm^{-1} belong to the C = N and C – N peaks, respectively, caused by the stretching vibration of the melamine ring. The peaks near 820, 1 034, 1 200 and 1 660 cm^{-1} are the vibrational absorption peaks of P – O, P – O – P, P = O and P – OH, respectively. The absorption peaks of the above infrared spectral features are consistent with the literature reports of MPP[16], indicating the target product.

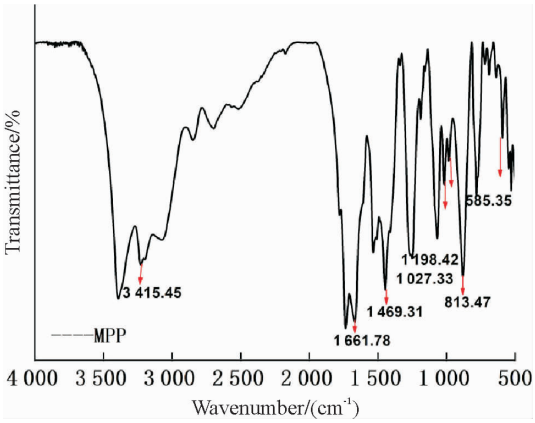


Fig. 3 FTIR spectra of MPP

3.1.2 EDS element analysis

The percentage of elements in MPP was analyzed by EDS spectroscopy, it can be seen from Table 2 that there is a difference between the actual value and the theoretical value in the percentage of elements in MPP, but the deviation was less than 1.5%, which proved that the synthesized product was the target product of MPP.

Table 2 The percentage of elements in MPP %

Element	Theoretical Value	Actual Value
C	43.22	42.98
O	17.13	16.76
P	16.14	15.56
N	19.53	20.65
H	3.98	4.05

3.1.3 TGA analysis

The thermal stability of MPP was test by TGA, which was carried out under nitrogen atmosphere from 50 ℃ to 700 ℃, the corresponding TGA and DTG data are shown in Fig. 4 and Table 3. The initial decomposition temperature (T_5%) of MPP is 311.0 ℃, the maximum decomposition temperature (T_{max}) is 410 ℃, the residual amount of MPP at 700 ℃ is 32.9%. The decomposed temperature of PVA is 230

℃ ~250 ℃[17], MPP's is higher than that of PVA, this stated that MPP was suitable for the preparation of flame retardant PVA hydrogel films.

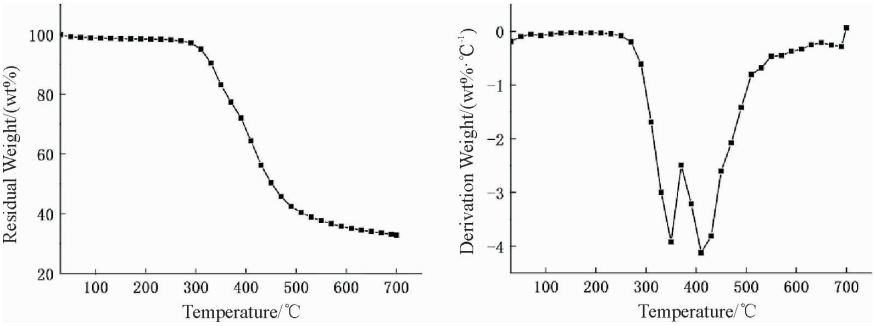


Fig. 4　The TGA curves of MPP under N_2

Table 3　TGA data of flame retardant PVA composite material under N_2

Samples	$T_{5\%}$ /℃	R_{max} /(% · min^{-1})	T_{max} /℃	Residue at 700 ℃/%
MPP	311.0	4.1	410.0	32.9

3.2　Interaction between PVA and MPP molecules

PVA was cross-linked with H_3BO_3 to form the PVA hydrogel films, in which the possible hydrogen bonds existing in the molecules had the －OH on the molecule chain of PVA formed hydrogen bond with the NH_2 on molecule structure of MPP, －OH on molecule chain of PVA formed hydrogen bond with P ＝O and P－OH on molecule structure of MPP, a schematic diagram of the hydrogen bond structure formed is shown as Fig. 5:

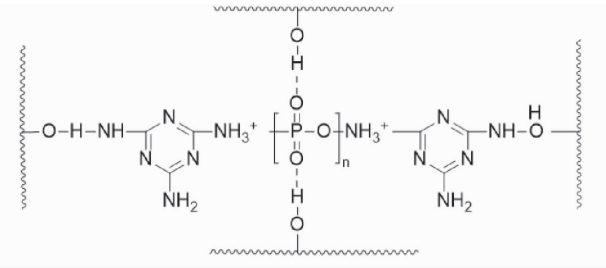


Fig. 5　The schematic diagram of the hydrogen bond structure formed in PVA /MPP hydrogel films

The hydrogen bond existing in the molecules was characterized by FTIR analysis, rheological behavior and mechanical properties of the PVA /MPP composite hydrogels.

3.2.1　FTIR analysis

Fig. 6 is the infrared spectras of the PVA and PVA/MPP composite hydrogels, it can be seen from Fig. 4 that a broader absorption peak appeared at 3 500 ~3 250 cm^{-1}, belonging to the hydroxyl group peak (－OH) of the molecular chain of PVA, due to the hydrogen bonding between －OH on the molecular chain of PVA and $-NH_2$ on the molecular structure of MPP, the stretching vibration absorption peak of the hydroxyl group (－OH) appeared red-shifted from 3 340 cm^{-1} to 3 241 cm^{-1}, with the increasing content of MPP, red shift degree was increased, indicating more intermolecular hydrogen bonds between MPP and PVA.

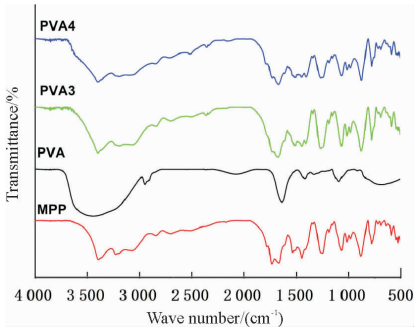


Fig. 6　FTIR spectra of PVA、PVA/MPP hydrogel films

3.2.2　Mechanical properties

The tensile properties of the flame retardant PVA and PVA/MPP hydrogel films were tested using a universal mechanical testing machine, and the specific mechanical properties are shown in Fig. 7. As shown in Fig. 7, the tensile strength did not change much after the addition of MPP, due to the hydrogen

bonding between –OH on the molecular chain of PVA and $-NH_2$ on the molecular structure of MPP, the interaction force between PVA and MPP is increased. However, the elongation at break decreased sharply from 7.5% to 2.9%, the reason may be that MPP was dispersed in the PVA hydrogel films and MPP formed stress concentration points, resulting in a decrease in elongation at break.

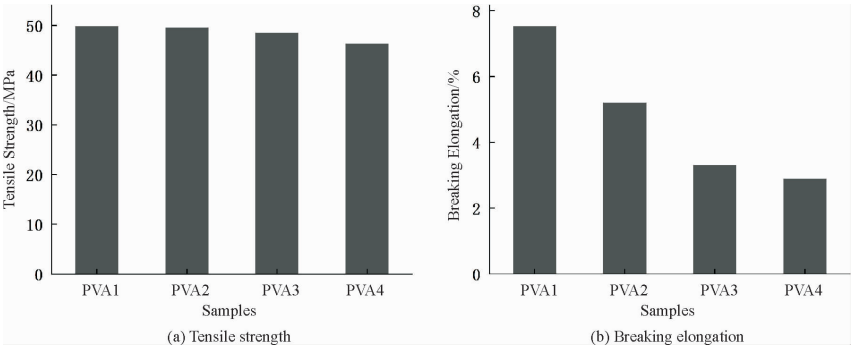


Fig. 7 Tensile strength and breaking elongation of flame retardant PVA /MPP hydrogel films

3.2.3 Rheological behavior

The rheological properties of the PVA/MPP hydrogel films were characterized by a rheometer, the curve of the energy storage modulus (G′), loss modulus(G″)with frequency are shown in Fig. 8, it can be seen from the figure that G′ exceeded G″, the change of G″ with frequency is not significant, which states the PVA composite hydrogels was behaving in a solid-like state[18-19], PVA crossed with H_3BO_3 to form a network structure, in which MPP formed hydrogen bonds with PVA, which strengthened PVA hydrogels, resulting in a solid-like behavior without the collapse of the structure. G′ of PVA/MPP hydrogel films increased with an increasing MPP content, hydrogen bonds interaction between MPP and PVA was enhanced, and so the strength of the PVA/MPP hydrogel films was improved.

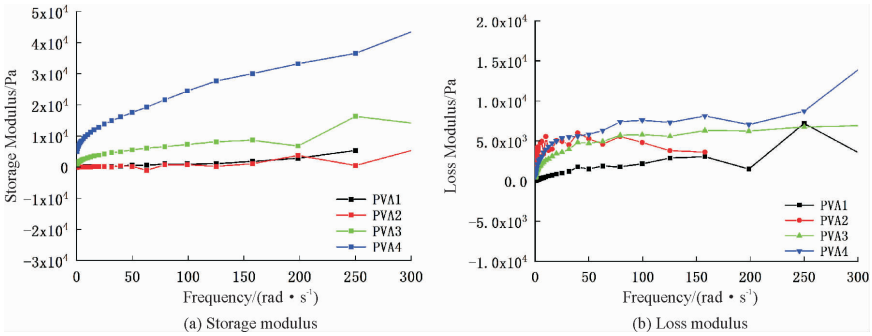


Fig. 8 Storage modulus and loss modulus of PVA/MPP hydrogel films

3.3 Flame retardant properties

3.3.1 TGA test

The thermal stability of the PVA/MPP hydrogel films was evaluated by TGA, and the relevant TGA curves and data are shown in Fig. 9 and Table 4. It can be seen that the $T_{5\%}$ of the PVA/MPP hydrogel films was higher than that of the PVA hydrogel films, increasing from about 81.5 ℃ to 119.5 ℃. T_{Max} was increased from 250.4 ℃ to 405.8 ℃, and the maximum decomposition rate was decreased from 14.0% to 3.7%, indicating that the addition of MPP can improve the thermal stability of the PVA hydrogel films. And the residual char of the PVA hydrogel film with different amounts of MPP at 700 ℃ was 31.5, 32.9 and 34.1% respectively, indicating that MPP can enhance the the residual char of the PVA hydrogel film while burning.

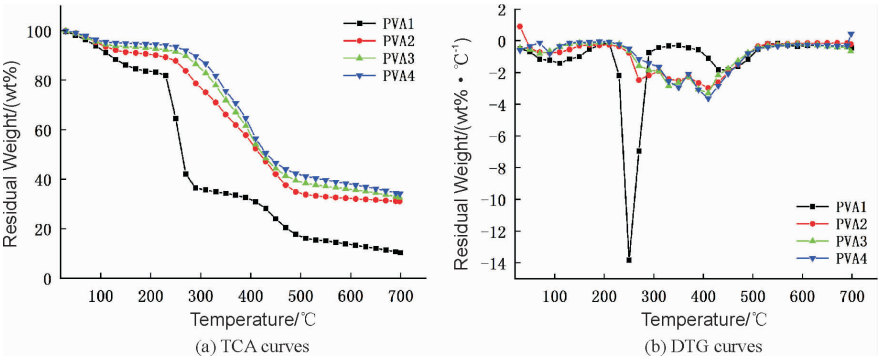


Fig. 9　TGA and DTG curves of the PVA/MPP hydrogel films

Table 4　TGA data of the PVA/MPP hydrogel films in N_2

Samples	$T_{5\%}$ /℃	R_{max} /(% · min^{-1})	T_{Max} /℃	Residue at 700 ℃/%
PVA1	81.5	14.0	250.4	10.4
PVA2	105.7	3.1	403.7	31.5
PVA3	100.0	3.6	403.5	32.9
PVA4	119.5	3.7	405.8	34.1

3.3.2　UL-94 testing

The UL-94 test results for the PVA /MPP hydrogel films are shown in Table 5. The PVA hydrogel film failed the flame retardant UL-94 test with dripping while burning. When MPP was added at 10 wt%, the PVA2 reached a UL-94 V-1rating, while at 20 wt% or 30 wt%, both PVA3 and PVA4 reached UL-94 V-0 rating. This suggests that MPP improved the flame retardant property of the PVA hydrogel film. It can be infered from the UL-94 test results that the minimum addition of MPP was 20 wt% for the PVA/MPP hydrogel films to reach a UL-94 V-0 rating.

Table 5　UL-94 results of the PVA /MPP hydrogel films

Samples	UL-94 test (3.2 mm)				
	t_1/s	t_2/s	Dripping	Ignite cotton	Rating
PVA1	15	14	Yes	Yes	NR
PVA2	12	6	No	Yes	V-1
PVA3	7	6	No	No	V-0
PVA4	6	9	No	No	V-0

3.3.3　CCT test

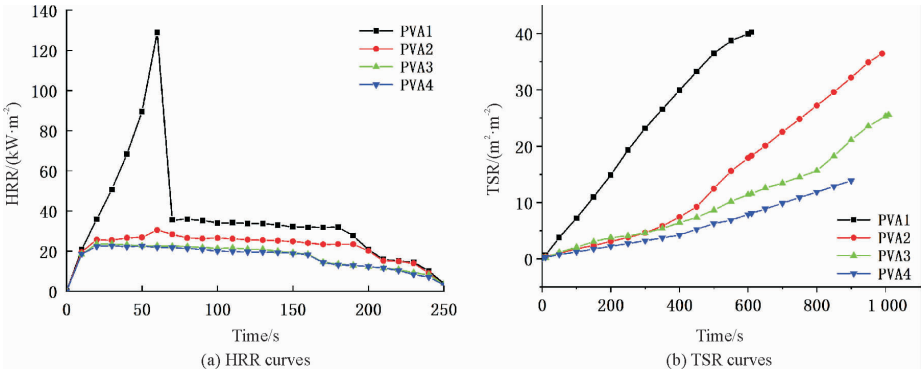
In order to evaluate the flame retardant properties of PVA/MPP hydrogel films, its burning behaviour was evaluated by CCT, the HRR and TSR curves are shown in Fig. 9 and the relevant CCT data are shown in Table 6. As shown in Table 6, according to TTI, the larger the TTI, the better the flame retardant for the PVA composite hydrogels, the PVA1 was inflammable with a large amount of heat when ignited within 111 s, the fire spread index (FGI)[20] was 2.10 kW · m^{-2} · s^{-1}, the fire growth index (FGI) can be calculated according to Table 6. FGI = PHRR/T, T- the time corresponding to the peak, which means a higher fire risk. Compared to the PVA1, the TTI of the PVA hydrogel film with the addition of MPP was prolonged from 431 s to 732 s, FGR decreased from 0.16 W · m^{-2} · s^{-1} to 0.14 kW · m^{-2} · s^{-1}, therefore, fire risk of the PVA hydrogel films combustion is greatly reduced.

Table 6　CCT data of the PVA/MPP hydrogel films

Samples	TTI /s	PHRR /(kW·m^{-2})	TTPHRR /s	TSR /(m^2·m^{-2})	FGR /(kW·m^{-2}·s^{-1})
PVA1	111	128.9	60	40.3	2.10
PVA2	431	30.5	180	36.4	0.16
PVA3	732	23.7	160	25.6	0.15
PVA4	498	22.7	160	13.9	0.14

Fig. 10(a) shows there was a reduction in HRR compared to the PVA1 after the addition of MPP, indicating that the addition of MPP can effectively improve the flame retardant property of PVA hydrogels. Fig. 10(b) shows the TSR curves of PVA/MPP hydrogel films. As shown in the figure, the PVA1 released a large amount of smoke in a short period of time. In addition, the thermal degradation time of PVA1 is longer than that of other samples. After addition of 10, 20 and 30 wt% of MPP, the TSR decreased from 36.4 to 13.9 m^2 · m^{-2}. During the

combustion process, the addition of MPP could effectively increase the density of char layer inhibiting volatile gases from breaking through the char layer and reduce the smoke release.

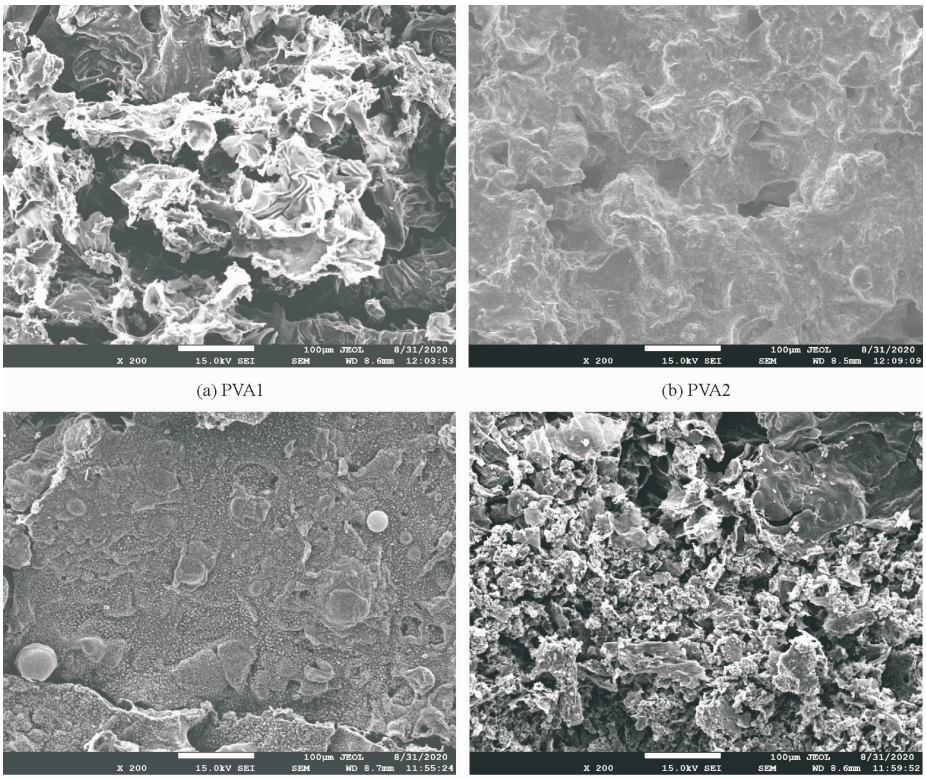


(a) HRR curves (b) TSR curves

Fig. 10 HRR and TSR curves of the PVA/MPP hydrogel films

3.4 Retardant mechanisms

Fig. 11 shows the SEM images of the residual char layer of the PVA/MPP hydrogel films after UL-94 testing. The PVA hydrogel film failed the UL-94 rating test, formed a loose and brittle char layer, which was not an effective char layer. However, the char layer of the PVA/MPP hydrogel films with 20 wt% MPP was denser, and the char layer of PVA4 became loose. The optimal amount of MPP to be added was 20 wt%. At this arnount, the PVA/MPP hydrogel film formed a sufficient protective char layer which interrupted the exchange of oxygen and energy with the outside. This result was consistent with the results of the UL-94 rating test.



(a) PVA1 (b) PVA2

(c) PVA3 (d) PVA4

Fig. 11 SEM images of char residues for PVA, PVA2, PVA3 and PVA4.

The pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) was applied to study the pyrolysis gaseous products of PVA and PVA/MPP hydrogel films. The main pyrolysis products of PVA hy-

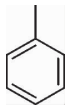
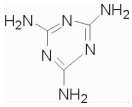
drogel film are listed in Table 7. The PVA hydrogel film mainly produced three kinds of pyrolysis products at 600 ℃, most of them were chain-like structures. Table 8 lists the main pyrolysis compounds of the PVA/MPP hydrogel films thermal cracking, of which the content of carbon dioxide (CO_2) and melamine was the highest. CO_2 diluted the concentration of flammable gas and oxygen, and took heat away, melamine was produced by the decomposition of MPP, which is a nitrogen-containing flame retardant, and in short, CO_2 and melamine acted as a gas-phase flame retardant mechanism.

Table 7　The main pyrolysis products of PVA hydrogel at 600 ℃

Label	T_R/min	Peak area /%	Molecular Structure	Molecular Formula
1	1.57	25.0		CH_3CHO
2	2.57	27.4		C_4H_6O
3	7.67	7.61		C_6H_8O

Compared with pure PVA hydrogel film pyrolysis products, the PVA/MPP hydrogel films products were mainly cyclic. It showed that the addition of MPP dehydrated to form cyclic compounds and promote the formation of a carbon layer.

Table 8　The main pyrolysis products of PVA /MPP hydrogel film at 600 ℃

Label	T_R /min	Peak area /%	Molecular Structure	Molecular Formula
1	1.50	59.7	O=C=O	CO_2
2	2.65	9.9		C_6H_6
3	4.18	2.1		C_7H_8
4	17.65	22.1		C_3H_6N

(1) MPP decomposed into phosphoric acid and melamine, and melamine is further decomposed to N_2 and CO_2, which acted as a gas-phase flame retardant mechanism;

(2) Phosphoric acid promotes the dehydration, cross-linking and cyclization of PVA to form a continuous and dense char layer, which played a part of condensed-phase flame retardant mechanism.

In a word, the flame retardant mechanism of PVA/MPP hydrogel films is the synergistic effect of gas-phase and condensed-phase flame retardant mechanisms, according to Py-GC-MS and related references[21-23]. Possible flame retardant mechanisms of the PVA/MPP hydrogel films are described in Fig. 12.

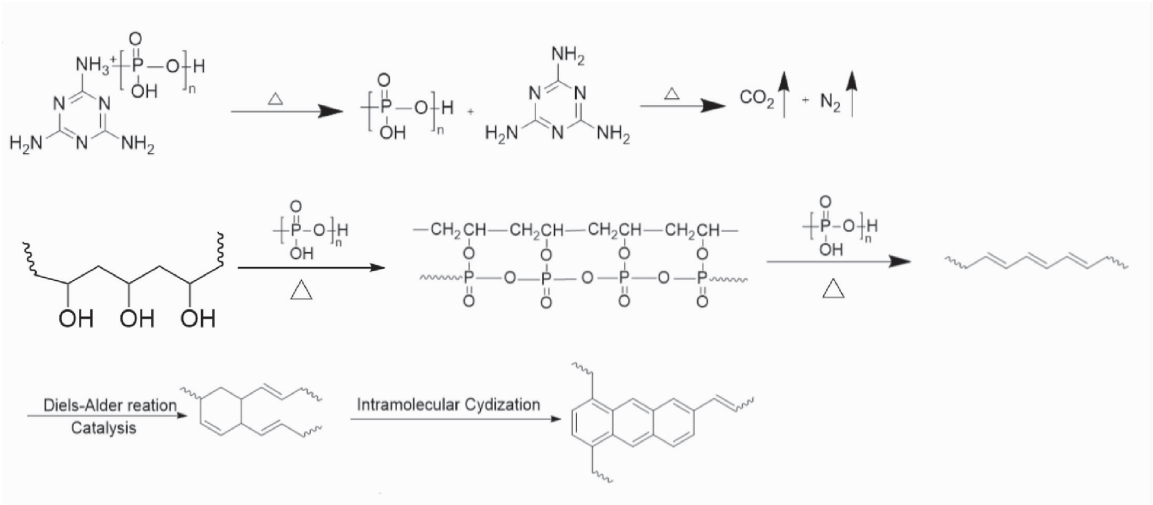


Fig. 12　Possible mechanisms of MPP flame retardant PVA hydrogel films

4 Conclusions

(1) MPP was synthesized using melamine and phosphoric acid, then added into PVA to prepare the flame retardant PVA hydrogel film via H_3BO_3, when addition of MPP was 20 wt%, the flame retardant properties of the PVA/MPP hydrogel films can reach UL-94 V-0 rating, also, MPP can effectively reduce the HRR and the smoke emission of the PVA hydrogel film.

(2) MPP decomposed to melamine and phosphoric acid, melamine further decomposed to N_2 and CO_2; Phosphoric acid promotes the PVA hydrogel films to form a continuous and dense char layer, the flame retardant mechanism of PVA/MPP hydrogel films is a synergistic effect of gas-phase and condensed-phase flame retardant mechanism.

(3) PVA cross-linked with H_3BO_3 forms PVA hydrogel film, in which PVA formed hydrogen bonds with MPP, which improves the flame retardant properties of PVA while maintaining the mechanical properties of PVA.

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