Preparation of aluminum hydroxide/aluminum phosphinate flame-retardant poly(vinyl alcohol) foam through thermal processing

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ABSTRACT: A novel flame-retardant poly (vinyl alcohol) (PVA) composite foam was prepared successfully through thermal processing, which was filled with high content of flame retardant, based on aluminum hydroxide (ATH) and aluminum phosphinate (AlPi) and using water as plasticizer and blowing agent. The flame-retardant property and mechanism of the prepared foam matrix were studied by vertical burning test, limiting oxygen index (LOI), cone calorimeter, scanning electronic microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The experimental results showed that the PVA/ATH/AlPi (1/1.2/0.05) composite achieved LOI value of 41% and UL94 V-0 (3.2 mm) rate. The addition of ATH and AlPi into PVA matrix significantly decreased flammability of the composites, because a more compact and continuous char layer of the PVA/ATH/AlPi composite could be formed, due to the involvement of AlPi in the char-forming reaction. Compared with the pure PVA sample, the peak heat release rate (PHRR) and total heat release (THR) of PVA/ATH/AlPi (1/1.2/0.05) composite were reduced by 76.5% and 58.2%, respectively. Built upon this PVA-based foam matrix with good flame retardancy, the flame-retardant PVA-based foam was successfully prepared through thermal extrusion. In addition, the influence of water content on melt viscosity, foam structure and mechanical strength was also analyzed. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42020.

INTRODUCTION

Polymeric foams have been widely applied in many important fields such as household industry, construction material, aerospace and medical treatment, and so on due to their excellent comprehensive properties, including good heat preservation, sound insulation and energy-saving performance, high specific strength, light weight and flexibility. However, polymeric foams are extremely flammable owing to their elemental composition (mainly consist of carbon and hydrogen) and porous structure [high porosity, thin pore wall, large surface area, and high content of air (∼98%)]. The fire disasters were frequently caused by the polymeric foams, which have brought serious threat to the security of human lives and properties. Thus, flame-retardant polymeric foams are urgently needed.

Generally, the flame-retardant property of the polymer foams such as polystyrene (PS), polyurethane (PU), and polyethylene (PE) can be improved by adding halogen flame retardants.[1–8] However, the use of halogen flame retardants should be gradually reduced, due to the release of some carcinogen such as dioxin, brominated furan during their combustion, resulting in

serious threat to the safety of humans and environment.[9] Therefore, it is significantly important to develop the novel polymer foams with environment-friendly (i.e., halogen-free) and intrinsic flame-retardant characteristics (i.e., the foam itself is nonflammable or the foam matrix can act as one part of the flame retardants), for example, melamine foam.[10]

When it is necessary to prepare some novel polymer foams, the poly (vinyl alcohol) foam has many superior properties, including the environment-friendly, good biocompatibility and biodegradability, excellent solvent resistance, and low cost,[11–13] which provide it with a wide application in biomedical, drug and packaging fields. More importantly, PVA is a macromolecular char forming agent, which may be directly prepared to be foam material with intrinsic flame-retardant characteristics.[14,15] In addition, PVA-based foam is mainly prepared by emulsion templating,[16] baking process,[17,18] and sol-gel methods.[19] Except for these methods, the thermal processing is a better approach to prepare PVA-based foam, which has some merits, such as continuous process, no need organic solvent, simplicity and economics. However, it is very difficult for PVA to be thermally

Table I. Formulation and Flame Retardancy of Samples

| Sample | The ratio of component | | | | UL94 classification | LOI (%) |
	PVA	H₂O	ATH	AlPi		
1	1	0	0	0	NR	19
2	1	0.5	0	0	NR	28
3	1	0.5	0.8	0	NR	35
4	1	0.5	1.1	0	NR	35
5	1	0.5	1.2	0	NR	38
6	1	0.5	1.2	0.01	V-2	38
7	1	0.5	1.2	0.02	V-2	39
8	1	0.5	1.2	0.05	V-0	41

NR, no rating.

processed, because it has high hydrogen bonding of intermolecular and intramolecular, and its melting temperature (about 230°C) is very close to the decomposition temperature (about 240°C). In our previous work, the thermal processing of PVA through using water as the plasticizer was successfully realized.[20–23] Moreover, the novel halogen-free flame-retardant PVA foams have been prepared successfully, in which PVA acted as foam matrix and macromolecular carbon source, melamine phosphate (MP) was used as flame retardants and nucleation agent, and the bound water in PVA acted as plasticizer, blowing agent, and synergistic flame retardant. The foams possessed the intrinsic flame-retardant characteristics based on PVA/MP composites through continuous thermal extrusion foaming and had excellent flame retardancy, reaching UL94 V-0, LOI 35%.[24]

Actually, MP has some limitations when it is used as flame retardant, for instance, higher price, smoke producing and unavailable for preparing highly filled foams. With environment-friendly property and low-cost, ATH is an inorganic flame retardant which has a comprehensive application as the filler for polymer material.[25] Thus, it could be an alternative of flame retardants for PVA foam. In addition, AlPi can be added to enhance the char forming of PVA in condensed phase, and the flame-retardant property of PVA will be improved further.

In this paper, the PVA/ATH-based flame-retardant foam was prepared successfully through thermal processing, in which water was acted as plasticizer and blowing agent, AlPi was the synergistic agent. The flame-retardant property and the possible mechanism of foam matrix were investigated, besides, the influences of water content on melt viscosity, foam structure and mechanical strength was also studied.

EXPERIMENTAL

Materials
Aluminum hydroxide (ATH) was purchased from Chengdu KeLong Chemical Co. Ltd, the particle size was about 20–30 μm. Aluminum phosphinate (AlPi) was furnished from Clariant (Shanghai, China). Poly(vinyl alcohol) (PVA), with a polymerization degree of 1700 and an alcoholization degree of 99%, was supplied by Sichuan Vinylon Corporation (Chongqing, China).

Preparation of PVA/ATH and PVA/ATH/AlPi Composites
The PVA particles were added into quantified water, and then the mixture of PVA particles and water were stored in an airtight container, which was placed at the room temperature until completely swollen, and then the plasticized PVA particles and ATH/AlPi were mixed in a high-speed mixer. Finally, the mixture were extruded in a single-screw extruder (RM-200C, Harbin Harpro electrical technology CO. LTD. Harbin China) and cut into pellets(The band heater temperatures for extruder barrel were 120, 180, 160, and 130°C in the hopper to die direction, the screw speed was 30 rpm). The components of different samples were listed in Table I.

Preparation of Flame-Retardant PVA Standard Specimen
The PVA/ATH and PVA/ATH/AlPi composites pellets obtained earlier were injection molded using an injection molding machine (MA 1200-SMS-A, Haitian Plastics Machinery LTD. Ningbo China) into standard specimens (The temperature distribution along the injection direction: 120, 180, 160, and 130°C, the injection pressure was 60 MPa) for vertical burning, LOI tests, according to ASTM D3801 and ASTM D2863, respectively.

Preparation of Flame-Retardant PVA/ATH/AlPi Composites Foam
The plasticized PVA particles with different water content and ATH/AlPi were mixed in a high-speed mixer, then the mixture were extruded using the single-screw extruder (RM-200C, Harbin Harpro electrical technology CO. LTD. Harbin China) into foam (The band heater temperatures for extruder barrel were 100, 170, 160, and 125°C in the hopper to die direction, the screw speed was 25 rpm).The composition of different samples were listed in Table III.

Characterization
UL94 classification: The vertical burning test was carried out by using the horizontal and vertical flame tester (Zhuhai Hua Ke Testing Equipment Co. Ltd) according to ASTM D3801. The dimensions of the samples were 127 mm × 12.7 mm × 3.2 mm and the specimens were pretreated under 25°C for 24 hr. The amount of water remaining is about 8.4% ± 0.5% for PVA sample and 7.5% ± 0.5% for flame-retardant PVA samples.

LOI test: The LOI test was conducted on the automatic oxygen index analyzer (Shandong Textile Science Research Institute) according to ASTM D2863. The dimensions of the samples were 120 mm × 6.5 mm × 3.0 mm and the specimens were pretreated under 25°C for 24 h. The amount of water remaining is about 8.4% ± 0.5% for PVA sample and 7.5% ± 0.5% for flame-retardant PVA samples.

Cone calorimetric analysis: The cone calorimetric analysis was measured by using the cone calorimeter (Fire Testing Technology Ltd) according to the ISO 5660 standard test method. The samples with a size of 100 mm × 100 mm × 4 mm were irradiated with a heat flux of 50 kW/m².

Scanning electron microscopy analysis: Scanning electron microscopy analysis was performed by using the scanning electron microscope (SEM, FEI, Eindhoven, the Netherlands). The micrographs of the composites and residue were obtained at 20 kV.
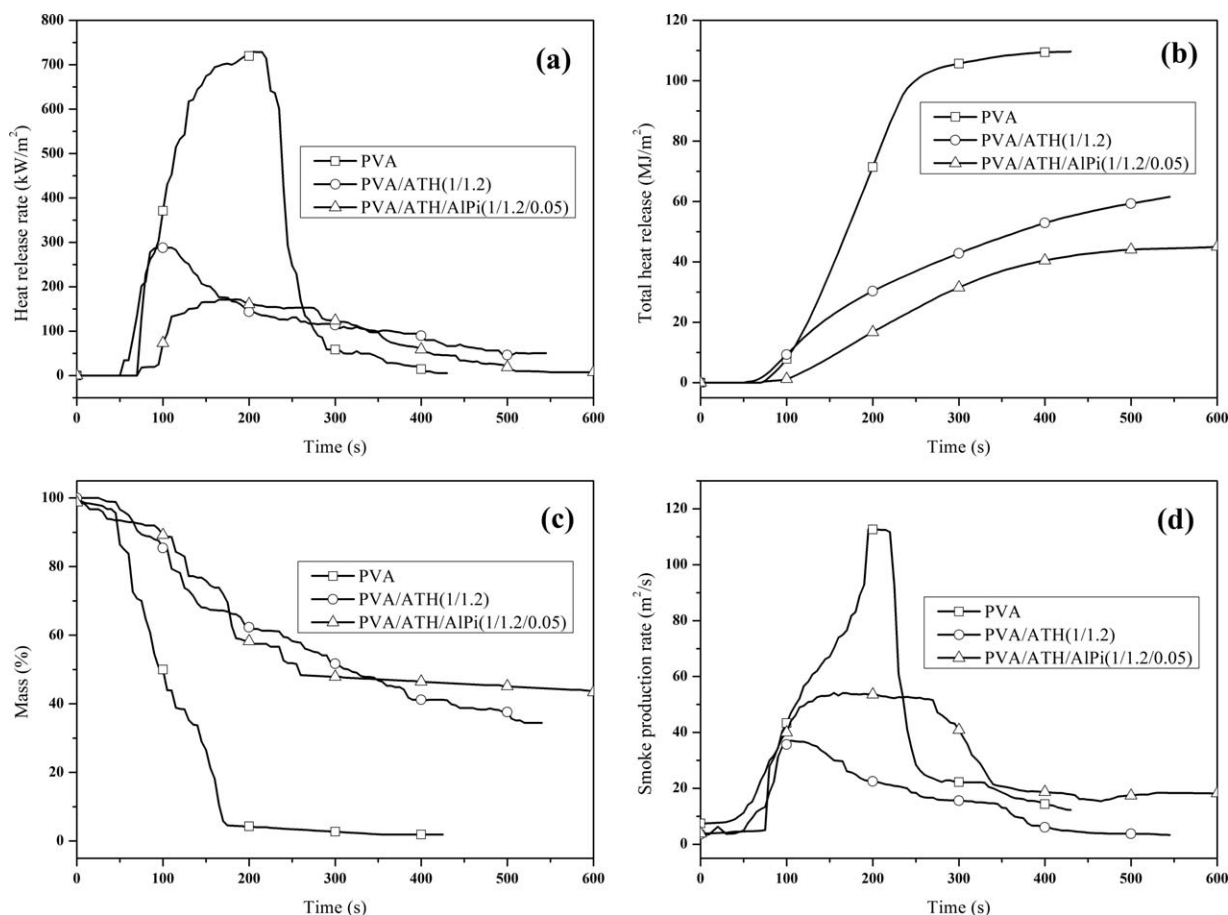
Figure 1. Cone calorimeter curves of the samples: (a) heat release rate; (b) total heat release; (c) mass loss; and (d) smoke production rate curves.

X-ray photoelectron spectroscopy analysis: The X-ray photoelectron spectroscopy (XPS) analysis was conducted on an Shimadzu/Kratos AXIS Ultra DLD Multifunctional X-ray Photoelectron Spectrometer (Manchester, UK). The compensation for charging all binding energies were referenced to C_{1s} at 285.0 eV and the possible deviation of the instrument was 0.1 eV.

Viscosity analysis: The melt viscosity of each sample was investigated by using torque rheometer (RM-200C, Harbin Harpro electrical technology CO. LTD. Harbin China) during extrusion (The band heater temperatures for extruder barrel were 100, 170, 160, and 125°C in the hopper to die direction.

Table II. Cone Calorimeter Data of the Samples

Sample	TTI (s)	PHRR (kW/m^2)	t_p (s)	AHRR (kW/m^2)	THR (MJ/m^2)	PSPR (m^2/s)
PVA	35	729	205	288	110	113
PVA/ATH(1/1.2)	55	288	100	107	62	37
PVA/ATH/AlPi (1/1.2/0.05)	60	171	185	74	46	54

TTI, time to ignition; PHRR, peak heat release rate; t_p, time to peak heat release rate; AHRR, average heat release rate; THR, total heat release; PSPR, peak smoke production rate.

Foam structure analysis: The extruded foam samples were examined by using SEM (FEI, Eindhoven, the Netherlands), the microstructure of fractured surface was achieved at 20 kV. The expansion ratio (Φ) of samples were calculated as the ratio of the volume of PVA-based composite (V_P) to the volume of PVA-based composite foam (V_f), here the foam strips were roughly viewed as cylinder, and its volume can be calculated through the formula: $V = \pi R^2 L$. So the composite and the foam were taken at the equal weight, and the expansion ratio can be calculated by the formula as follows:

$$\Phi = \frac{V_f}{V_P}$$

The cell density (N) was determined by the number of cells per unit volume, and the number of cells per cubic centimeter was calculated as follow:

$$N = \left(\frac{n}{A}\right)^{\frac{3}{2}} \times \Phi$$

where n is the number of cells in a defined area (A).[26,27]

Mechanical performance analysis: the mechanical properties of extruded foam sample were tested by using a universal testing machine (model RG L-10, Shenzhen Reger Instrument Co.).
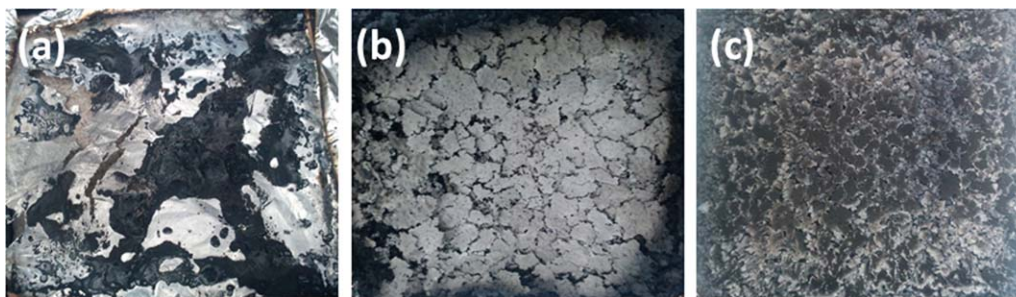
Figure 2. The residue of the samples after combustion: (a) PVA, (b) PVA/ATH(1/1.2), and (c) PVA/ATH/AlPi(1/1.2/0.05). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Tensile strength which was defined as the maximum stress it could be subjected to before fracture.

RESULTS AND DISCUSSION

Flame-Retardant Property of PVA/ATH/AlPi Composites

The LOI and vertical burning tests (UL-94) were used to investigate the flame retardancy of the samples, and the results were showed in Table I.

From Table I, it can be seen that blank sample 1 was extremely flammable, and its LOI was only 19%. When water was used as plasticizer, the LOI value of sample 2 reached 28%, much higher than that of sample 1. As we know that there are three kinds of water in PVA/water system: non-freezing water, freezable bound water and free water.[28–32] During the combustion process, the water, especially the non-freezing water and free water in the plasticized PVA specimens would release and evaporate which will absorb a large amount of heat from the combustion zone and dilute the oxygen and flammable gas, resulting in the increase of LOI value. Therefore, the water in the plasticized PVA could be considered as the synergistic flame-retardant agent.

As shown in Table I, when ATH was added into the plasticized PVA, the LOI value of the sample further increased to 38% at the ratio of 1.2 for ATH (sample 5). This could be attributed to that ATH could absorb heat and dilute gas concentration by releasing crystal water during the combustion process, and more importantly, the added ATH can decrease the fuel amount in condensed phase by replacing PVA matrix. Unfortunately, we found that the PVA/ATH samples could not reach any rate in UL94 standard.

It is well known that PVA contains large amount of hydroxyl groups and is a good char agent when the acid source exists. Thus, it is possible that the flame-retardant property of PVA/ATH composites can be improved by adding organic phosphate. Here, aluminum phosphinate (AlPi) was selected as synergistic flame-retardant agent. As shown in Table I, when the ratio of AlPi was only 0.05, the flame retardancy of the sample was improved significantly and reached UL94 V-0 and the LOI value of 41%.

The cone calorimeter was also used to estimate fire safety of the flame-retardant PVA composites. Figure 1 showed the heat release rate (HRR) curves, total heat release (THR) curves, mass loss curves and smoke production rate (SPR) curves of PVA, PVA/ATH (1/1.2) and PVA/ATH/AlPi (1/1.2/0.05) composites. The corresponding data summarized from cone calorimeter curves were listed in Table II.

As shown in Figure 1(a), there was a steep peak at about 2 min after ignition for PVA sample, releasing a large amount of heat in a short time, while the peaks of PVA/ATH and PVA/ATH/ AlPi were much smaller, indicating that heat was released at a very low speed. From Table II, the PHRR of pure PVA was 729 kW/m^2, while the PHRR of PVA/ATH and PVA/ATH/AlPi were significantly decreased by 60.5% and 76.5%, respectively. The THR of pure PVA was 110 MJ/m^2, and the THR of PVA/ATH and PVA/ATH/AlPi decreased by 43.6% and 58.2%, respectively. The PSPR of PVA/ATH and PVA/ATH/AlPi composites decreased by 67.3% and 52.2%, respectively, compared with the pure PVA, indicating that ATH can also play an important role in inhibiting the production of smoke. As shown in Figure 1(c), the mass loss rate of PVA/ATH and PVA/ATH/AlPi were much slower than that of pure PVA. More importantly, their residue was also enhanced, and the residue of PVA/ATH and PVA/ATH/AlPi increased to 34.5% and 43.4%, while the residue of pure PVA was extremely low (only 1.9%). Besides, the alumina content in the PVA/ATH and PVA/ATH/AlPi residue are 29.1% and 28.5% respectively when we consider that ATH is fully decomposed into alumina, then we subtract the alumina content from the residue and we can get the char content of PVA/ATH and PVA/ATH/AlPi are 5.4% and 14.9%, respectively. This relatively higher char content of PVA/ATH/AlPi indicates that AlPi can play a catalytic action in the char forming reaction.

The residues of the samples after combustion were further investigated, as shown in Figure 2. It can be seen that almost no residue was left after combustion of pure PVA [Figure 2(a)]. For PVA/ATH sample [Figure 2(b)], even though a larger amount of char was observed, the residue was un-continuous cracks. This suggests that most of the residue could be the decomposed product of ATH (i.e., Al$_2$O$_3$), and there was no an effective char layer formed in PVA/ATH samples. For PVA/ATH/ AlPi sample [Figure 2(c)], the compact and continuous char layer was obtained. The phenomena further supported the result of a better flame retardancy of PVA/ATH/AlPi sample than the other samples (Table I). Actually, it has been recognized that char formation is of great significance in improving the flame-retardant properties of polymer materials.[33]

Flame-Retardant Mechanism of PVA/ATH/AlPi Composites

To further explore the flame-retardant mechanism of ATH and AlPi in PVA/ATH/AlPi composites, the elements composition and chemical bonds of the residue of the samples after
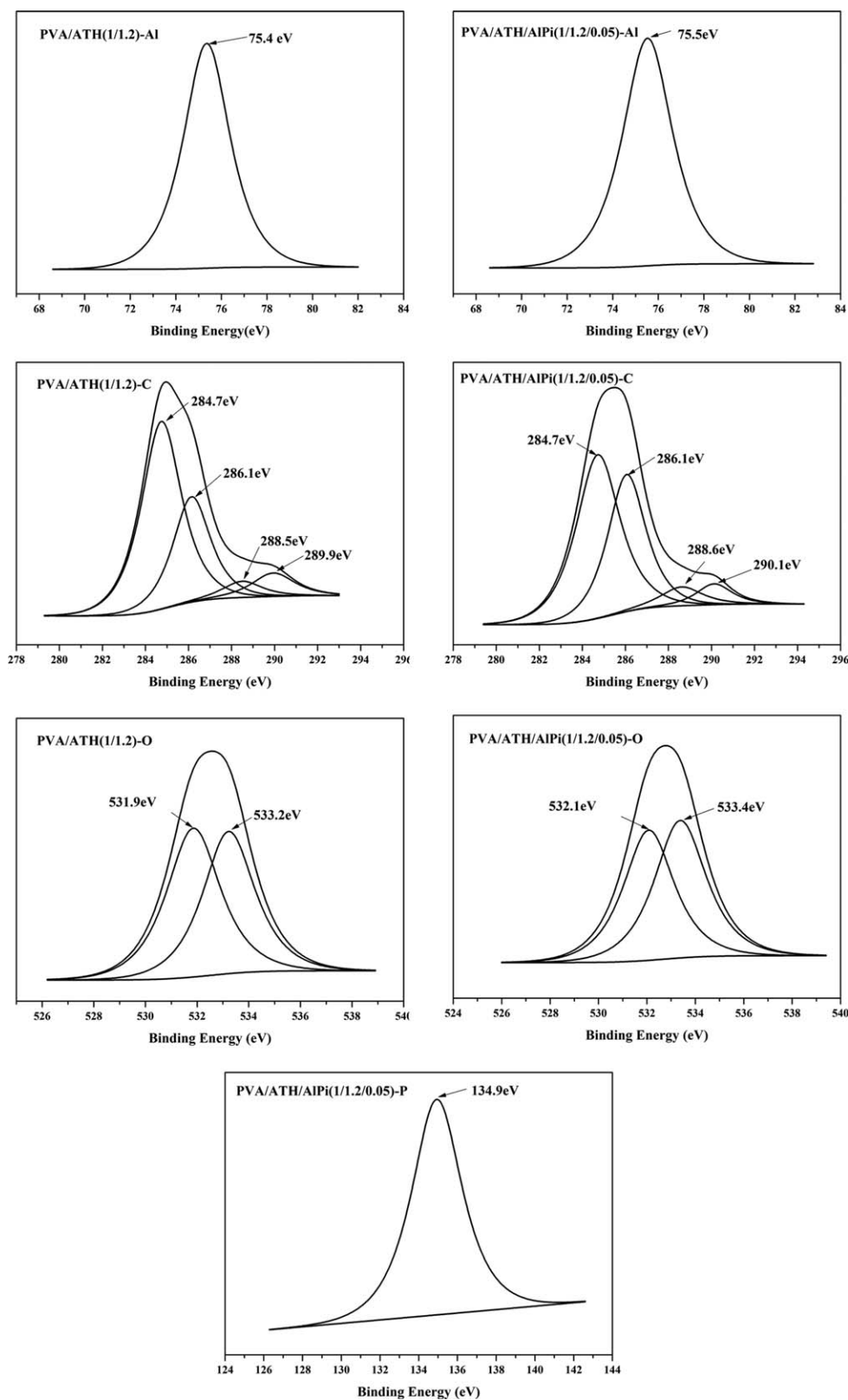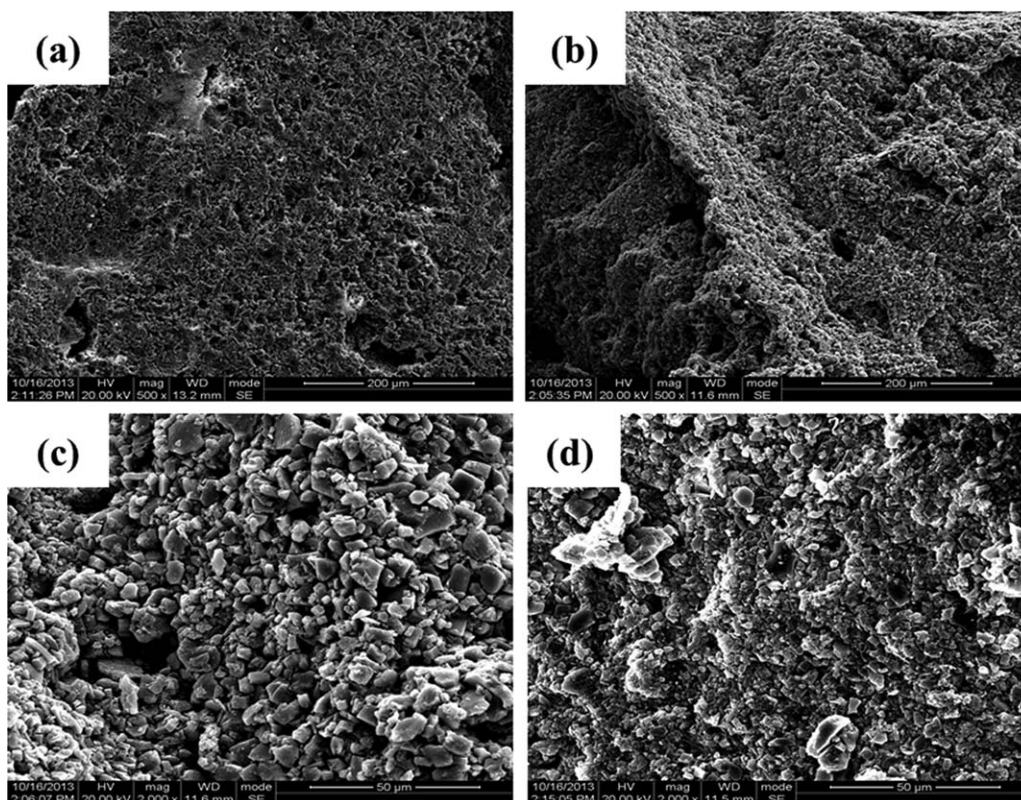
Figure 3. XPS spectra of the residue after cone calorimeter.

combustion were investigated. Figure 3 showed XPS spectra of C_{1S}, O_{1S}, P_{2P}, and Al_{2P} for PVA/ATH (1/1.2) and PVA/ATH/AlPi (1/1.2/0.05) composites, respectively.

From the spectra of PVA/ATH, it can be seen that C_{1S} spectrum has four bands with binding energy at 284.7 eV, 286.1 eV, 288.5 eV and 289.9 eV, respectively. The C_{1S} peak at 284.7 eV can be

Figure 4. SEM images of the residue after cone calorimeter (a, c) PVA/ATH(1/1.2) and (b, d) PVA/ATH/AlPi(1/1.2/0.05).
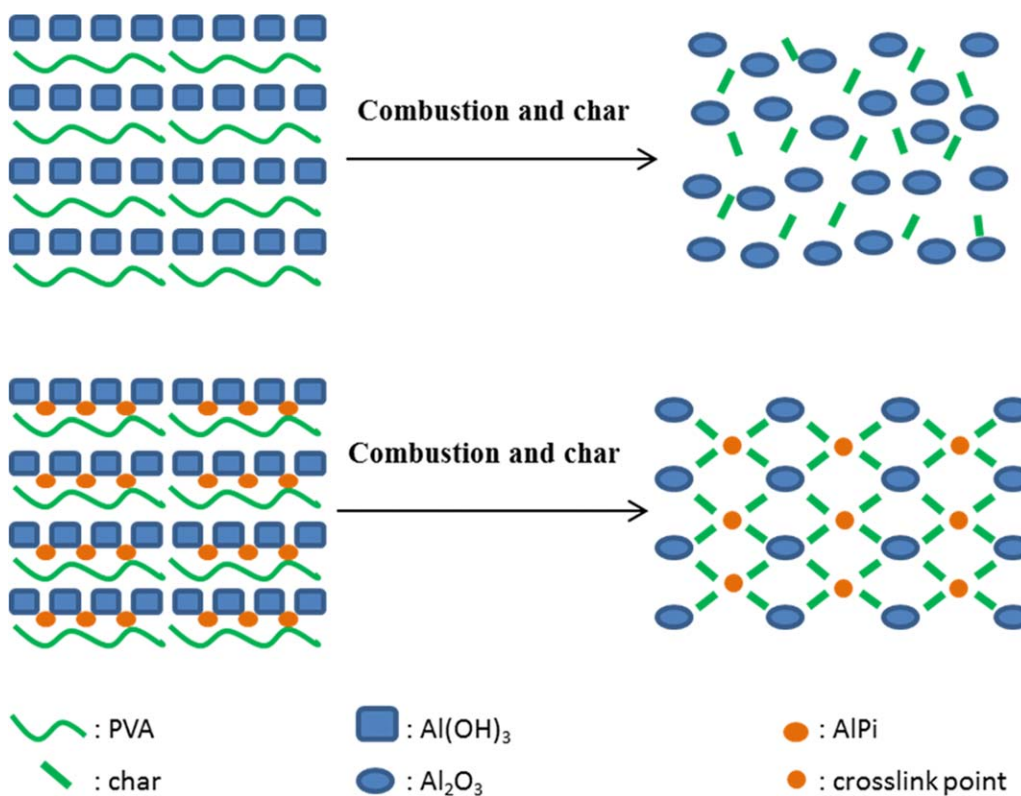
Figure 5. The model of char forming of PVA/ATH and PVA/ATH/AlPi samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
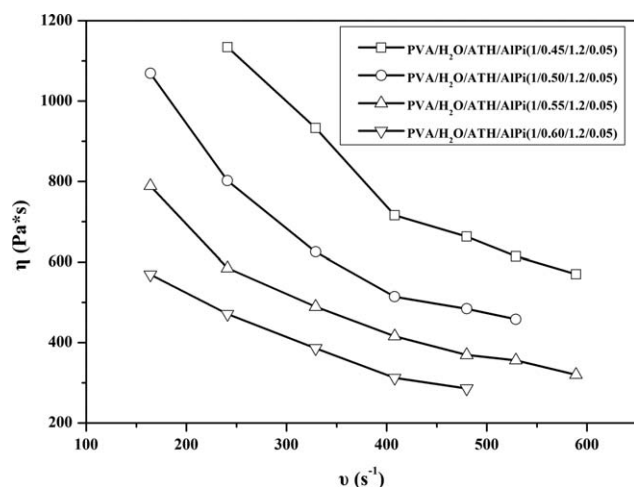
Figure 6. The viscosity curves of samples with different water content.

assigned to the C—C and C—H groups in aliphatic and aromatic structure. The C_{1S} peaks at 286.1 eV–288.5 eV can be assigned to the C—O and C=O groups in some products of the thermal oxidative degradation. The C_{1S} peak at 289.9 eV can be assigned to O=C—O group in ester. O_{1S} spectrum exists two bands with binding energy at 531.9 eV and 533.2 eV, which can be assigned to C—O—C group and C=O group respectively. Al_{2P} spectrum only has one band with binding energy at 75.4 eV, indicating the formation of Al_2O_3.

From the spectra of PVA/ATH/AlPi, C_{1S} spectrum also has four bands, and the C_{1S} peak at 284.7 eV is the same as that of PVA/ATH, the peaks at 286.1 eV–288.6 eV show a shift by 0.1 eV to higher energy direction, which can be assigned to the additional group C—O—P. Another shift by 0.2 eV to higher energy direction also occurs to the peak at 290.1 eV, which can be assigned to the extra group O=C—O—P. O_{1S} spectrum exists two bands, which shift to 532.2 eV and 533.4 eV, which can be assigned to C—O—P, P—O—P and P=O, respectively. There is only one band in P_{2P} spectrum, which can be assigned to C—O—P in phosphate.[34–36] The peak in Al_{2P} spectrum shifts from 75.4 eV to 75.5 eV, which indicates the possible existence of Al-O-P group in residue of PVA/ATH/AlPi composite.

The relative content of four different kinds of C can be obtained by calculating the peak area. The relative content of C at 284.7 eV, 286.1 eV, 288.6 eV, and 290.1 eV are 57.4%, 30.2%, 4.9%, and 7.6% in the residue of PVA/ATH composite, and 51.4%, 37.7%, 5.6%, and 5.3% in the residue of PVA/ATH/AlPi composites. Element carbon in residue exists mainly in the form of

C—C and C—O, nearly 90% of total content. For PVA/ATH/AlPi composites, the content of C—C decreased to 51.4% from 57.4% and the content of C—O increased to 37.7% from 30.2% in PVA/ATH composites. It indicates that AlPi could catalyze and participate in the char forming reaction of PVA.

The morphology of the residue for PVA/ATH and PVA/ATH/AlPi was investigated by SEM, as shown in Figure 4. At the 200 μm scale, the residue of PVA/ATH composite showed loose and porous, while that of PVA/ATH/AlPi appeared more compact and continuous At the 50 μm scale, it was observed clearly that the residue of PVA/ATH was made up with micropore particles, existing obvious surfaces among the particles. It could be inferred that the residue was randomly piled up with Al_2O_3 particles, without any connection among them, resulting in the loose and porous structure in the residue of PVA/ATH. However, we can see that the residue of PVA/ATH/AlPi has distinctly different morphology with the compact and continuous structure, indicating that the Al_2O_3 particles jointed together, forming a continuous plane.

Based on above analysis, the model of char forming for flame-retardant PVA sample was established (Figure 5). It can be conceived that the Al_2O_3 particles were randomly dispersed in the residue of PVA/ATH system. However, during the combustion process of PVA/ATH/AlPi system, AlPi participated in the Char forming reaction, and the Al_2O_3 particles jointed together via connecting point AlPi and formed crosslink network structure. Eventually, a compact and uniform residue was achieved, which provided an excellent barrier.

Foam Structure of PVA/ATH/AlPi Composite Foam
The addition of ATH and AlPi endued PVA/ATH/AlPi composite with good flame-retardant property, and the flame-retardant PVA/ATH/AlPi composite foam was successfully prepared through thermal extrusion. However, PVA/ATH/AlPi foam cannot obtain the comparative flame-retardant effect because of its porous structure. In addition, it is also a challenge to achieve the PVA-based foam with high quality cell structure using water as the blowing agent.

The melt viscosity is an important parameter for polymer foam during the extrusion foaming, which has to be strong enough to prevent the collapse and rupture during the bubble growth, and a good quality foam structure usually occurs with a relatively high melt viscosity.[37] The plasticizer content (water) has a significant influence on the melt viscosity of plasticized PVA system, and its effect was investigated by using torque rheometer during extrusion.
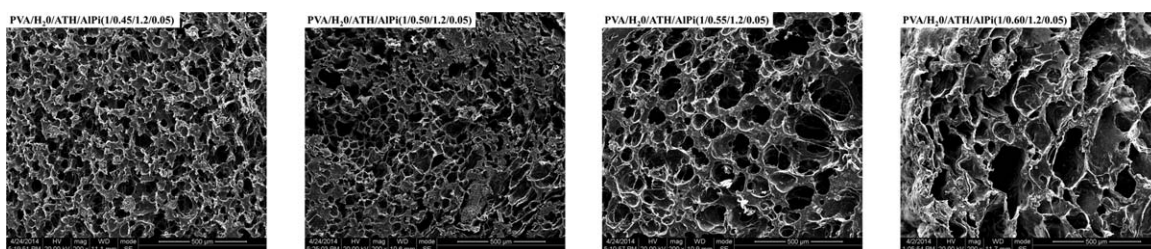
Figure 7. The foam structure of samples with different water content.

Table III. Foam Structure Parameters of Flame-Retardant PVA Composite Foams

| Sample | The ratio of component | | | | Foam density (g/cm^3) | Expansion ratio | Cell density (10^3/cm^3) | Cell size (μm) |
	PVA	H$_2$O	ATH	AlPi				
9	1	0.45	1.2	0.05	0.18	14.06	68,883.8	71.1
10	1	0.50	1.2	0.05	0.29	10.56	48,325.9	72.3
11	1	0.55	1.2	0.05	0.31	4.62	5966.4	105.1
12	1	0.60	1.2	0.05	0.36	3.06	2327.8	119.14

Figure 6 showed the viscosity of the samples with different water content at various shear rates. It can be seen that the low water amount and low shear rate resulted in the higher melt viscosity during extrusion.

Figure 7 was the effect of water on the foam structure of PVA/ATH/AlPi (1/1.2/0.05). Some foam parameters were listed in Table III. It was evident that a higher cell density and smaller cell size were achieved at the low water concentration. Generally, the increasing concentration of blowing agent results in a higher cell density because of a greater driving force to nucleate bubbles. However, the blowing agent (water) was also used as the plasticizer in the system, and its plasticizing effect can significantly decrease the melt strength. As the result of that, the expansion ratio of samples decreased with the increase of water content because of the weaker melt viscosity. Sample 12 with high water concentration appeared severe collapse and rupture in the process of extrusion foaming. On the other hand, the samples with strong viscosity can maintain the foam structure when a large number of bubbles formed instantaneously. However, the samples with lower water content were not conducted in this experiment, because the minimum water concentration in plasticized PVA system is 1/0.45, which can make the highly filled PVA composite prepared through thermal processing successfully.

Finally, the mechanical performance of flame-retardant PVA foam was also studied, and the corresponding results were listed in Table IV. With the decreasing water content, the tensile strength and elastic strength improved rapidly while the elongation reduced slowly. The sample with a better foam structure obtained the tensile strength of 7.25 MPa and elastic strength of 151.62 MPa.

Table IV. Mechanical Properties of Flame-Retardant PVA Composite Foams

Sample	Tensile strength (MPa)	Elastic strength (MPa)	Elongation at break (%)
9	7.25	151.62	22.3
10	4.25	92.94	39.3
11	1.65	34.31	42.0
12	0.67	5.52	44.7

CONCLUSIONS

A novel flame-retardant PVA/ATH/AlPi composite foam was prepared successfully through thermal processing. The PVA/ATH/AlPi composite achieved the LOI value of 41% and UL94 V-0 (3.2 mm) rate. The PVA/ATH/AlPi composite showed a more compact and dense char layer than PVA/ATH composite after combustion, resulting from the involvement of AlPi into the char-forming reaction. Compared with the PVA sample, the PHRR and THR of PVA/ATH/AlPi (1/1.2/0.05) composite were reduced by about 76.5% and 58.2%, respectively.

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