Efficient Approach to Improving the Flame Retardancy of Poly(vinyl alcohol)/Clay Aerogels: Incorporating Piperazine-Modified Ammonium Polyphosphate

Yu-Tao Wang, Shi-Fu Liao, Ke Shang, Ming-Jun Chen, Jian-Qian Huang, Yu-Zhong Wang,*,[†] and David A. Schiraldi*,[‡]

[†]Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, State Key Laboratory of Polymer Materials Engineering, National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), Sichuan University, Chengdu 610064, China

[‡]Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, United States

ABSTRACT: Ammonium polyphosphates (APP) modified with piperazine (PA-APP) was used to improve the flame retardancy of poly(vinyl alcohol) (PVA)/montmorillonite (MMT) aerogels, which were prepared via an environmentally friendly freeze-drying method. The thermal stabilities of the samples were evaluated by thermogravimetric analysis (TG); the flammability behaviors of samples were investigated by limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter (CC) tests. TG test results showed that the 5% weight loss temperature ($T_{5\%}$) of PVA/MMT/PA-APP was 10 °C higher than that of PVA/MMT/APP. In combustion testing, all of PVA/MMT/PA-APP aerogels achieved V-0 ratings and have a higher LOI values than the unmodified PVA/MMT aerogel. Moreover, the aerogel with 1% PA-APP$_5$, which means that the content of piperazine is 5% in PA-APP, decreased the cone calorimetry THR value to 5.71 MJ/m^2, and increased the char residue to 52%. The compressive modulus of PVA/MMT/PA-APP was increased by 93.4% compared with PVA/MMT/APP because of the increase in interfacial adhesion between matrix and PA-APP fillers. The densities of the PVA/MMT/PA-APP samples were slightly lower than those of the unmodified aerogels because of reduced shrinkage in the presence of PA-APP. All the tests results indicated that the incorporation of PA-APP not only improved the thermal stability and flame retardancy of aerogels but also maintained their mechanical properties.

KEYWORDS: aerogel, poly(vinyl alcohol), ammonium polyphosphate, piperazine, flame retardant, mechanical behavior
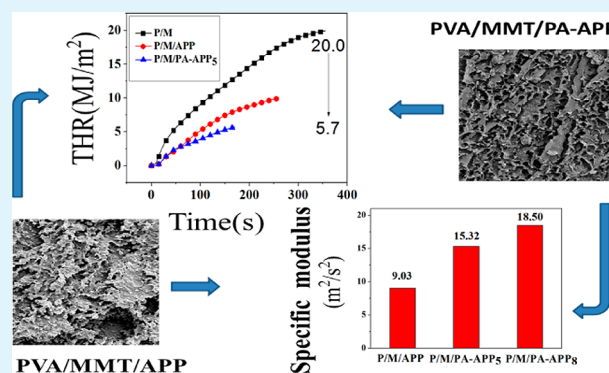
1. INTRODUCTION

Aerogels, one of the lightest families of materials known in the world, were first reported by Kistler in the early 1930s. Silicon alkoxides, such as Si(OCH$_3$)$_4$ and Si(OC$_2$H$_5$)$_4$, were used as precursors,[1,2] followed by a sol−gel process, aging and drying. To avoid capillary pressure that would collapse the fine structures, supercritical drying has been widely used, although the production costs are high. This family of materials has attracted wide attention over seven decades, because of its unique set of properties, including low densities (ranging from 0.005 to 0.1 g/cm^3), high porosities and specific surface areas, and extremely low thermal conductivities.[3]

Clay-based aerogels have been actively studied more recently.[4−7] Montmorillonite clay (MMT) aerogels, first described by Mackenzie and Call, exhibit very poor mechanical behaviors because of their fibrous structures. Inorganic−organic hybrid aerogels have been developed and exhibit higher toughness and strengths than inorganic (mainly silica) aerogels.

To enhance their "gel skeletons" and improve their compressive strengths and moduli, we introduced water-soluble polymers or fibers into clay aerogels. A wide range of organic polymers can be used, including alginate,[8] casein,[9,10] poly(vinyl alcohol),[11−13] branched poly(ethylene imine),[14] poly(amide-imide),[15] and natural rubber.[7,16,17] These relatively low cost/low thermal conductivity hybrid porous materials can be prepared via an environmentally friendly freeze-drying method.[18,19] Traditional polymer foams can be replaced by polymer/clay aerogels in insulation and packaging areas.[4,11,20]

Poly(vinyl alcohol) is a good candidate for preparing aerogels because of its strong interaction with clays via hydrogen bonding and its high solubility in water. However, the flammability of PVA limits its applications in some significant

Table 1. Mechanical Properties and Densities of Aerogel Samples with APP and PA-APP

	P/M/APP	P/M/PA-APP$_4$	P/M/PA-APP$_5$	P/M/PA-APP$_7$	P/M/PA-APP$_8$
modulus (MPa)	0.91 ± 0.04	1.12 ± 0.14	1.44 ± 0.15	1.60 ± 0.09	1.78 ± 0.14
density (g/cm^3)	0.101 ± 0.001	0.097 ± 0.001	0.094 ± 0.002	0.095 ± 0.002	0.096 ± 0.002

fields. To improve the fire performance of PVA aerogels, researchers have recently carried out a significant body of work.[21−26] Some efficient commercial flame retardants, such as ammonium polyphosphate (APP), which have been shown to improve the flame retardancy of PVA, have been evaluated in PVA-based aerogels.[27] The addition of APP, however, decreased the mechanical properties of PVA aerogels while reducing their flammability. The dispersion of inorganic APP in the organic PVA matrix destroyed the pore structure of aerogel, thereby reducing the structural value of the foamlike aerogel.

Ammonium polyphosphate modified with piperazine (PA-APP) was first reported as a novel monocomponent intumescent flame retardant in our laboratory.[28] After being chemically modified by PA, this simple organically modified APP could potentially increase the interfacial adhesion of polymer matrix in hybrid aerogels opening the possibility of improved flame retardancy without loss of mechanical properties. In present work, PA-APP was added into the PVA/clay aerogel system to increase the interfacial adhesion between matrix as described above, and apparent density, mechanical properties, microstructure, thermal stability, and flammability were characterized.

2. EXPERIMENTAL SECTION

2.1. Materials. Poly(vinyl alcohol) (PVA) with a degree of polymerization of 1000 and a saponification degree of 99 mol % were purchased from Kelong (Chengdu, China). The clay Closite Na (Na+-MMT; PGW grade, cation-exchange capacity (CEC) equal to 145 mequiv/100 g, density 2.6 g/cm^3, was supplied by Nanocor Inc. Piperazine-modified ammonium polyphosphate (PA-APP) used in this study was fabricated in accordance with our previous work.[28] Four different types of PA-APP were used in the present study: PA-APP$_4$, PA-APP$_5$, PA-APP$_7$, and PA-APP$_8$, correspond to piperazine contents in PA-APP of 4, 5, 7, and 8%, respectively.

2.2. Preparation of Aerogels. All of the aerogel composites were prepared from aqueous mixtures that consisted of 5 wt % PVA, 5 wt % MMT, and 1 wt % flame retardants. For example, to produce P/M/PA-APP$_4$ aerogels, where letter P denotes PVA and letter M refers to MMT, 10 g of Na+-MMT, 2 g of PA-APP$_4$, and 100 mL of deionized water were well-mixed at a high speed of 10 000 rpm, in a A-55 stirrer (Inayou,China) for 10 min. Simultaneously, 10 g of PVA was added into 100 mL of deionized water at 80 °C, stirring for 4 h. Then the aforementioned PVA solution (100 mL, 10%) were mixed with clay and the PA-APP$_4$ mixture and stirred for 2 h. The resulting gels were poured into a poly(tetrafluoroethylene) mold and frozen in a liquid nitrogen bath (−190 °C) immediately. The frozen samples were transferred to the freeze-dryer (VFD-1000, Beijing Bo Kang Experimental Medical Instrument Co.) for solvent sublimation. The aerogels were dried in vacuum oven, with a temperature of 80 °C, prior to characterization. This final product was denoted as P/M/PA-APP$_4$. Other samples were identified as P/M/APP, P/M/PA-APP$_5$, P/M/PA-APP$_7$, and P/M/PA-APP$_8$ and were prepared by a similar method. P/M aerogel were also prepared as a control.

2.3. Characterization. The apparent densities of the aerogels were calculated by measuring the mass and dimension using balance and digital calipers; three samples were tested for each composition and their values averaged. Compression testing was characterized on a universal testing machine (Model 4302, Instron Engineering Corporation), fitted with a 10 kN load cell, tested at a rate of 15 mm/min, and a maximum strain of 75%. Testing specimens measuring 18 mm in height and 20 mm in diameter were used; three samples

were tested for each composition and their values averaged. Morphological microstructure of the aerogels was investigated using a JEOL JSM 5900LV scanning electron microscopy (SEM)(JEOL, Japan) at the accelerating voltage of 20 kV. A TG 209F1(NETZSCH, Germany) was used to study the thermal stabilities of aerogels.The samples were heated from 40 to 700 °C at a heating rate of 10 °C/min under the nitrogen flow of 50 mL/min. The LOI values were performed using an HC-2C oxygen index meter (Jiangning, China) in accordance with ASTM D 2863−2009. The size of the specimens tested was 120 mm × 10 mm × 10 mm. The UL-94 vertical burning level was obtained with a CZF-2instument (Jiangning, China) in accordance with GT/T 8333−2008, and evaluating 125 mm × 10 mm × 10 mm specimens. The combustion behaviors of the aerogel were carried out by a cone calorimeter device (Fire Testing Technology, UK). The specimens (100 × 100 mm) with an average thickness of 10 mm were exposed to a beaming cone at a heat flux of 50 kW/m^2.

3. RESULTS AND DISCUSSION

3.1. Apparent Density and Mechanical Behavior. Table 1 lists the compressive moduli and densities of flame-retarded PVA aerogels prepared for this study. The densities of P/M/PA-APP aerogels ranged from 0.094 to 0.097 g/cm^3, lower than that of the P/M/APP control. The P/M/PA-APP aerogels exhibited less volume shrinkage during the freeze-drying process, leading to their lower densities (greater final volumes). The compressive modulus of P/M/APP averaged 0.91 ± 0.04 MPa, less than those observed with the P/M/PA-APP aerogels. Although the mechanical properties of P/M/APP aerogels were reported to decrease with increasing levels of flame retardant, attributed to poor interfacial adhesion between PVA and inorganic matter,[25] mechanical properties of P/M/PA-APP aerogels actually increased with increasing PA content in PA-APP. The compressive modulus of P/M/PA-APP$_8$ was 1.78 ± 0.14 MPa, nearly double that of the P/M/APP aerogels. The results imply that P/M/PA-APP aerogels could have stronger interfacial adhesion than P/M/APP aerogels.

Figure 1 shows the changes in specific compressive modulus with different PA content in PA-APP. The specific compressive modulus of the aerogels was computed by the ratio of ultimate
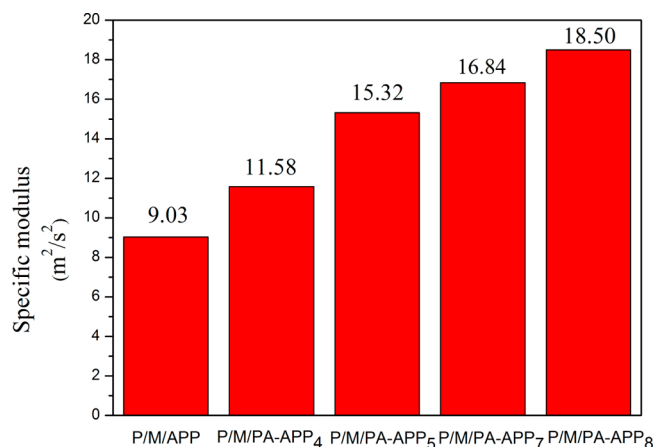

Figure 1. Specific compressive moduli of aerogel samples with APP and PA-APP.
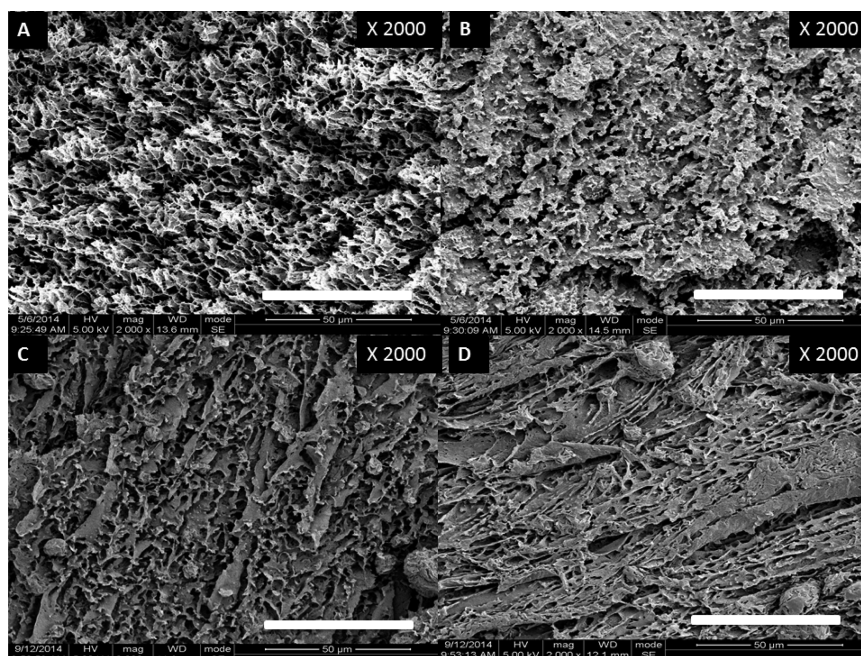
Figure 2. SEM images of aerogel samples. (A) PVA/MMT, (B) PVA/MMT/APP, (C) PVA/MMT/PA-APP$_7$, and (D) PVA/MMT/PA-APP$_8$ (scale bar: 50 μm).

compressive modulus to the density, and can better illustrate the mechanical character of aerogels by removing density differences from the comparison.[29] The values in Figure 1 and Table 1 demonstrate an increase in compressive properties after using PA-APP instead of APP. With increasing PA content in PA-APP, the specific compressive modulus of the aerogel increased. While the modulus of the P/M/PA-APP increased with additive levels, an optimal PA content in PA-APP can be expected, maintaining mechanical properties and maximizing flame retardance of the aerogel.

3.2. Microstructures of Aerogels. The morphologies of the P/M aerogels, P/M/APP aerogels, and a series of P/M/PA-APP aerogels are shown in Figure 2. It has been reported that P/M aerogels can form a three-dimensional network structure because of the strong hydrogen bonding interactions between MMT and PVA.[30] Figure 2A illustrates the three-dimensional network structure of P/M aerogels, whereas in Figure 2B that structure is substantially destroyed as a result of the addition of APP, presumably because of the reduction compatibility between polymer matrix and inorganic fillers. However, from Figure 2C, D, it is obvious that the PVA phase is linking between the different clay layers as a "bridge". A more complete pore structure has been formed in P/M/PA-APP aerogels, which is similar to the three-dimensional network structure of P/M aerogel—we attribute this to good compatibility between PA-APP and the polymer matrix, a system that does not limit rearrangements of PVA molecular chains and MMT platelets, thereby creating an orderly lamellar architecture instead of a damaged network structure.

3.3. Thermal Stability. The thermal properties of PVA-based aerogels were evaluated by thermogravimetric analysis (TGA; Figure 3) and differential thermogravimetry (DTG; Figure 4). The decomposition temperatures at 5% mass loss ($T_{d5\%}$), 20% mass loss ($T_{d20\%}$), and at maximum decomposition rate (T_{dmax}) are exhibited in Table 2. Besides, the values at maximum mass decomposition rate (dW/dT) and the residue amount are also presented. It can be observed that the first
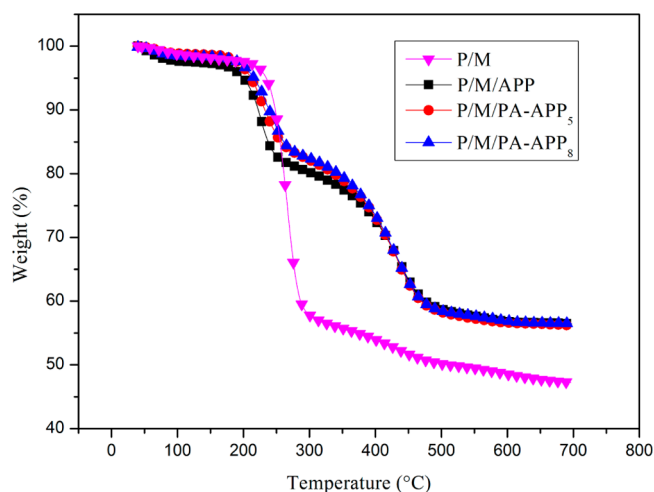

Figure 3. TG curves of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APPs at a heating rate of 10 °C/min under nitrogen.

weight loss stages, which appeared below 100 °C, are attributed to the removal of water because there are abundant surface hydroxyl groups in this aerogel system. The main step of weight loss, occurring between 200 to 500 °C, can be attributed to the decompositions of PVA and flame retardant agents. In this temperature region, PA-APP begin to decompose to produce polymeric phosphoric acid and N−P−C structures, whereas the NH_3 and H_2O are released at the same time.[28,31] Cross-linking of PVA hydroxyl groups with the phosphoric acid would be expected, as well as catalysis of esterification reactions by MMT to form a dense charred layer, which in turn would prevent the further decomposition of PVA chains.

Compared with P/M aerogel, the aerogels with PA-APP have a lower onset decomposition temperature ($T_{d5\%}$) because of the disintegration of fire retardants around 200 °C. However, the residue amount of aerogels with PA-APP is higher than that of P/M aerogel since cellular charred layers are formed on the
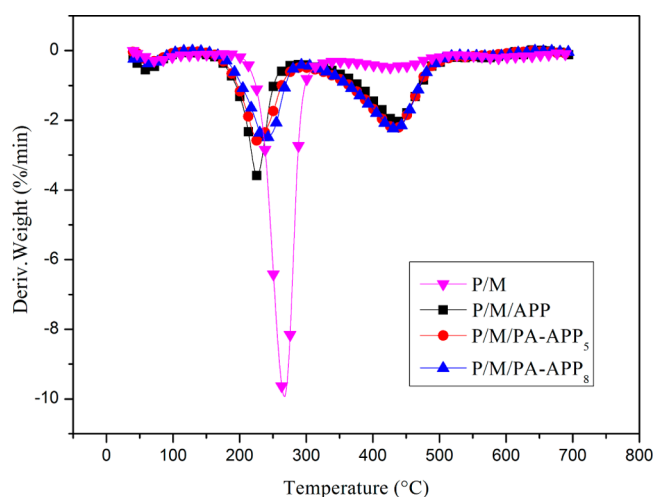
Figure 4. DTG curves of PVA/MMT, PVA/MMT/APP ,and PVA/MMT/PA-APPs at a heating rate of 10 °C/min under nitrogen.

Table 2. TGA Data of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APP Aerogels

samples	$T_{d5\%}$ (°C)	$T_{d20\%}$ (°C)	T_{dmax} (°C)	dW/dT (%/min)	residue (%)
P/M	235	261	268	10.2	47
P/M/APP	200	306	226	3.59	56
P/M/PA-APP$_4$	213	351	236	2.83	58
P/M/PA-APP$_5$	212	337	228	2.66	56
P/M/PA-APP$_7$	213	332	247	2.77	55
P/M/PA-APP$_8$	215	344	236	2.53	57

surface of aerogel to limit the further decomposition by the synergistic effect of PA-APP and MMT. Moreover, with the addition of PA-APP, the onset decomposition temperature ($T_{d5\%}$) and the temperature at maximum decomposition rate (T_{dmax}) of the P/M aerogel increased beyond that of the P/M/APP aerogel. At temperatures below 400 °C, the rate of weight loss of the P/M/PA-APP aerogels was lower than that of the P/M/APP aerogel as well. It was reported that PA-APP could produce more C=C and P−N−C structures during the decomposition than APP; this could result in a charred layer, which could in turn hinder heat transfer and prevent further decomposition.[28,32] The aerogels with PA-APP clearly exhibited superior thermal stability among the compositions evaluated in the present study.

Because of the different content of piperazine in PA-APP compositions, the corresponding aerogels exhibited slightly different thermal stabilities. Among the five aerogels tested, all of the P/M/PA-APP aerogels show the similar initial decomposition temperature ($T_{d5\%}$) at around 212 to 215 °C. Although P/M/PA-APP$_7$ demonstrated the highest temperature at maximum decomposition rate (T_{dmax}) and P/M/PA-APP$_4$ presented the highest char residue.

3.4. Combustion Behavior. The limiting oxygen index (LOI) values and vertical burning tests (UL-94) were carried out, evaluating flame-retardant performances of the samples, and the data are shown in Table 3. With the addition of flame retardants, the LOI values of aerogels increased significantly. However, compared with P/M/APP, the LOI values of P/M/

Table 3. LOI and UL-94 results of PVA/MMT, PVA/MMT/APP and PVA/MMT/PA-APP aerogels

samples	LOI (%)	UL-94
P/M	24.5	V-0
P/M/APP	42.0	V-0
P/M/PA-APP$_4$	38.5	V-0
P/M/PA-APP$_5$	36.5	V-0
P/M/PA-APP$_7$	36.3	V-0
P/M/PA-APP$_8$	34.0	V-0

PA-AAP were reduced. With the increase in percentage of PA in APP, the LOI values of aerogels drop slightly, perhaps because the PA-APP has a lower ignition temperature than APP and there are fewer acidic sites in APP after modification with piperazine.[28] All of the samples did achieve the V-0 rating in the UL-94 tests, likely as a result of the physical barrier effect of MMT.

Cone calorimetry is widely used in investigating the combustion performance of polymers and can offer plentiful data including the time to ignition (TTI), time to peak of heat release (tp), peak of heat release (pHRR), heat release rate (HRR), total heat release (THR), smoke produce rate (SPR), and total smoke production (TSP). The relevant data for the samples in this study are given in Table 4 and the data of P/M aerogels are listed as controls.

Table 4. Cone Calorimeter Data of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APP Aerogels

sample	TTI (s)	pHRR (kW/m^2)	TTPHRR (s)	FIGRA (KW/s.m^2)	THR (MJ/m^2)	Residue (%)
P/M	3	209.6	15	14.0	20.0	46.2
P/M/APP	6	88.4	20	4.4	9.6	49.7
P/M/PA-APP$_4$	6	80.4	20	4.0	10.0	48.2
P/M/PA-APP$_5$	7	88.5	20	4.4	5.7	52.0
P/M/PA-APP$_7$	4	106.6	15	7.1	11.1	40.6
P/M/PA-APP$_8$	6	94.2	20	4.7	11.5	51.3

Although all the samples are easily ignited under the test conditions of 50 kW/m^2, the addition of PA-APP or APP can increase the ignition time. Figure 5 displays the HRR curves of the aerogels; it is obvious that the HRRs of P/M/PA-APP aerogels decreased compared with the P/M aerogel. The pHRR (Table 4) of P/M aerogels was measured to be 210 kW/m^2, but with addition of P/M/PA-APP decreased to around 100 kW/m^2. The sample of P/M/PA-APP$_4$ exhibited the lowest pHRR among all the samples probably because of its high char barrier effect. Because of the rupture of the initial charred layer during the combustion, the P/M/PA-APP$_7$ and P/M/PA-APP$_8$ exhibit two HRR peaks.

As shown in Figure 6, the total heat release of P/M/PA-APP aerogels was dramatically reduced when compared with the control samples. The PVA/MMT aerogels have a THR data about 20 MJ/m^2, compared to a value of 5.7 MJ/m^2 for P/M/PA-APP$_5$ aerogels (which exhibit the lowest THR data among a series of P/M/PA-APP samples). The decrease of THR in P/M/PA-APP$_5$ aerogel is likely caused by the incomplete combustion phenomenon within the aerogels. With the addition of PA-APP$_5$ in P/M aerogels, more stable charred
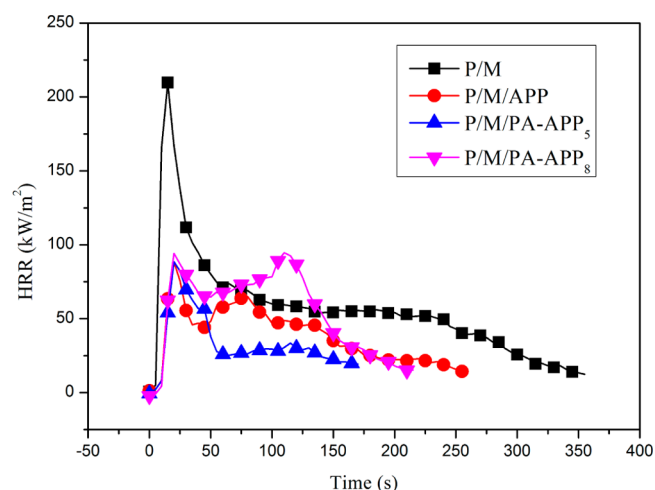
Figure 5. HRR plots of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APP aerogels.

Figure 6. THR curves of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APP aerogels.

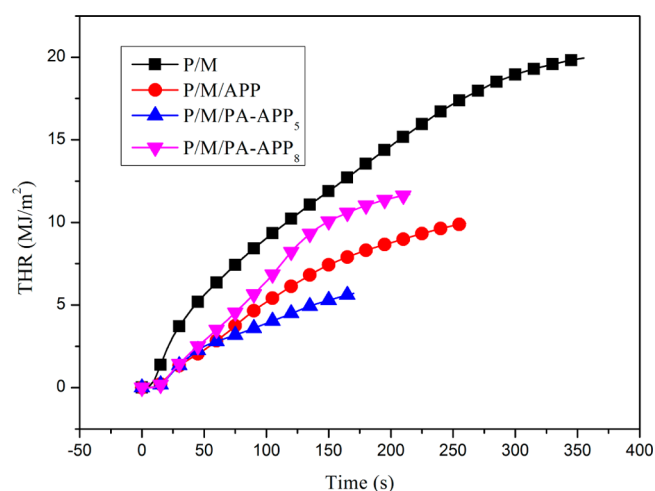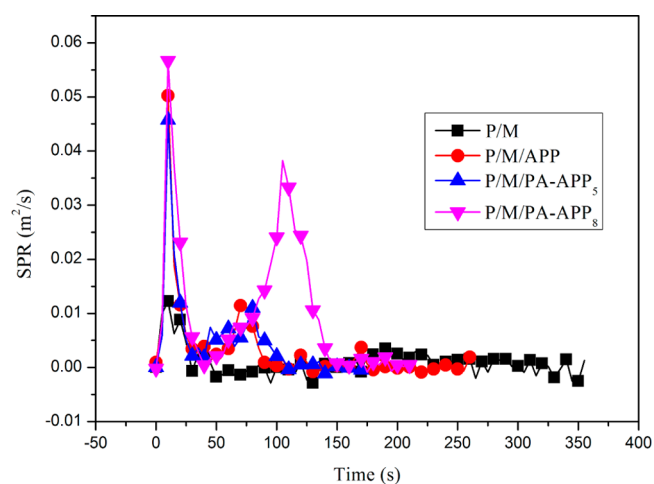**Figure 7.** SPR plots of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APP aerogels.
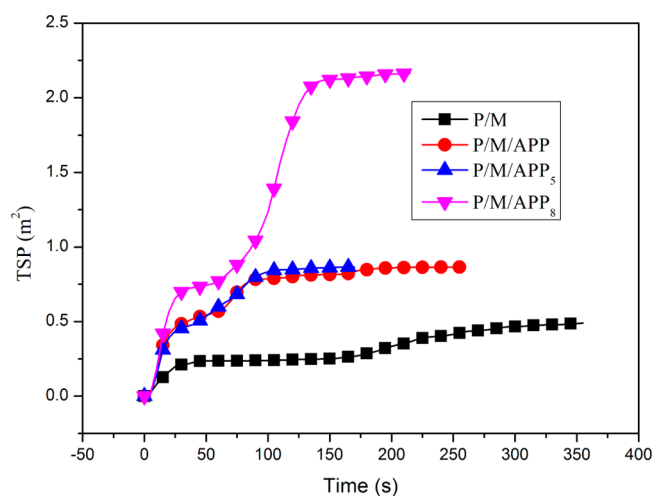
Figure 8. TSP curves of PVA/MMT, PVA/MMT/APP, and PVA/MMT/PA-APP aerogels.

layers are developed, which can prevent the discharge of combustible materials and gas during the combustion process.

Figures 7 and 8 illustrate the SPR and TSP curves during burning, respectively. It can be shown that the SPR and TSP increase with the addition of PA-APP, in all likelihood as a result of increased production of NH_3, NO, and other gases during the combustion; it was previously reported[28] that PA-APP emits significant amounts of NH_3 and H_2O during its thermal decomposition.

The fire growth rate (FIGRA) of samples is given in Table 4. FIGRA is a key parameter used to assess the risk of the fire, and is calculated by the following equation FIGRA = PHRR/t_p.[33] Materials which have a lower FIGRA exhibit higher flame retardancy (i.e., lower flammability) and the flashover time of the material can be delayed as well. For the P/M/PA-APP$_5$ aerogels, the FIGRA values significantly decreased from 14 to 4, compared with P/M composites, suggestive of increased survival chances under room fire conditions.

The mechanism of PA-APP fire retardation in PVA/MMT aerogels is expected to be similar to that of ammonium polyphosphate in PVA/MMT aerogels. With the decomposition of PA-APP, polymeric phosphoric acid and N−P−C structures are produced while the NH_3 and H_2O are released;

esterification of PVA hydroxyl groups with the polyphosphoric acid is also expected. Finally, combined with MMT, the structures like P−N−C and C=C form stable char layers, which plays a part as an insulation layer to prevent further decomposition of aerogels. The piperazine acts as an origin of char and it can help to form a denser char layer to reduce the THR (like the P/M/PA-APP$_5$ aerogel) during the combustion. However, with the increase in the piperazine content in PA-APP, the content of polymeric phosphoric acid decreased and fewer polymeric phosphoric acid was decomposed by PA-APP during the combustion. Obviously, it will become a disadvantage to form cellular char layers. Hence, the combustion behavior of P/M/PA-APP$_8$ is not as good as P/M/PA-APP$_5$.

4. CONCLUSIONS

PVA/MMT aerogels with APP or PA-APP were prepared by an environmentally friendly freeze-drying method. The apparent densities, mechanical properties, microstructures, thermal stabilities and flame retardancy of the hybrid aerogels were determined. Compared with P/M/APP aerogels, aerogels produced with PA-APP have greatly enhanced compressive properties, likely due to increased interfacial adhesion between

matrix and fillers. Compressive performance changes with the different modified amount of PA in PA-APP; P/M/PAA-APP$_8$ aerogels exhibit the highest compressive moduli among the test. SEM images demonstrated that P/M/PA-APP aerogels have more complete pore structures than are observed in P/M/APP aerogels. The incorporation of PA-APP slightly decreased the densities of the samples. TGA tests demonstrated increased onset decomposition temperatures for P/M/PA-APP aerogels, compared with their P/M/APP analogs. Combustion tests show slightly decreased LOI values of P/M/PA-APP aerogels, probably due to the lower amounts of acid in APP after modification with piperazine. There is also a great increase in LOI values compared with P/M control sample and all of the P/M/PA-APP aerogels can achieve V-0 rating. Cone calorimetry showed that the HRR and THR of P/M/PA-APP aerogels are much lower than the P/M control sample although the SPR and TSP increased because of more gases emitted. Moreover, the sharp reduction of the FIGRA values indicates that this aerogel composite will have a better performance during fire disasters. Further investigation should find the appropriate PA content in PA-APP to fit practical applications.

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: yzwang@scu.edu.cn
*E-mail: David.Schiraldi@case.edu

Notes
The authors declare no competing financial interest.

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