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Preparation and Flammability of Poly(vinyl alcohol) Composite Aerogels

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ABSTRACT: Poly(vinyl alcohol) (PVOH)-based aerogel composites with nanoscale silica, halloysite, montmorillonite (MMT), and laponite were prepared via a freeze-drying method. The PVOH/MMT and PVOH/laponite composites exhibit higher compressive moduli than the PVOH/SiO_2 or PVOH/halloysite samples. Layered microstructures were observed for the samples except with PVOH/laponite, which showed irregular network morphologies. Thermogravimetric analysis of the aerogel samples showed increased thermal stability with the addition of nanofillers. The heat release measured by cone calorimetry, smoke release, and carbon monoxide production of the aerogel composites are all significantly decreased with the addition of nanofillers; these values are much lower than those for commercial expanded polystyrene foam. The fillers did not lead to obvious increases in the limiting oxygen index values, and the corresponding time to ignition values decrease. The ability to adjust the nanofiller levels in these foamlike aerogel composites allows for specific tuning of these products for fire safety.

KEYWORDS: *aerogel, flammability, poly(vinyl alcohol)*

INTRODUCTION

Silica aerogels were first reported by Kistler in the early 1930s, making use of sol−gel hydrolysis of silicon alkoxides, such as $Si(OCH_3)_4$, $Si(OC_2H_5)_4$ and $SiO_n(OC_2H_5)_{4-2n}$.[1,2] Gel preparation, aging, and drying are the main steps for the preparation of such materials, with drying of the aerogel being the final and most critical step in the production process. To avoid capillary pressure, which causes collapse of the wet gel structure, supercritical drying is often used to produce these aerogels, although ambient-pressure drying has also been reported.[3] Aerogels produced in such a process possess extraordinarily low densities (~3 kg/m^3), are generally nonflammable and nonreactive, but, however, exhibit very poor mechanical properties and very high production costs.[4−7]

The preparation of montmorillonite clay (MMT) aerogels by freeze-drying of clay hydrogels was reported by Mackenzie[8] and Call;[9] the resultant fibrous structures exhibit poor mechanical properties overall. We have previously reported that MMT, laponite, and synthetic fluoromica can be freeze-dried to produce materials with properties improved over those of the original clay aerogels.[10] The incorporation of a wide range of polymers, including poly(vinyl alcohol) (PVOH), natural rubber, casein, pectin, and alginate, into these clay aerogels has led to a robust family of composites with densities in the range of 0.03−0.2 g/cm^3, produced using an environmentally benign process and bearing a striking resemblance to polymer foams, cork, and balsa wood.[11−19]

The use of inorganic nanofillers, layered particles like MMT and laponite, fibroid particlelike halloysite, and spherical particlelike nanoscale silica in environmentally friendly flame-retardant packages in polymer products has been widely attempted with mixed results.[20−27] It is proposed that the nanofillers act as thermal insulators and present a mass-transport barrier to oxygen and the flammable volatiles generated during polymer degradation;[28−30] Lewin has suggested that the accumulation of clay on the burning/gasifying material's surface results also from migration of the nanofillers because of their lower surface free energies compared with carbon-based polymers.[31,32] Clay particles have been demonstrated to play a catalytic role in the promotion of a char-forming reaction because the confined, superheated environment caused by layered silicates would trap decomposition products, making additional carbonization pathways available.[33−35] A very limited literature currently exists discussing the flammability of polymer/clay composite aerogels; the initial reports on this topic show these materials to exhibit extremely low flammability, generally superior to that of traditional polymer foams, with which they compete in the marketplace.[19,36−40]

In the present study, PVOH composite aerogels produced using different nanofillers were fabricated through the above-

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Table 1. Mechanical Properties of PVOH-Based Aerogels: Modulus in MPa, Density in g/cm^3, Specific Density (M/d) in MPa·cm^3/g

	PVOH	PVOH/MMT	PVOH/laponite	PVOH/halloysite	PVOH/SiO$_2$
modulus	3.8 ± 0.6	3.2 ± 0.3	4.1 ± 0.6	1.3 ± 0.2	2.9 ± 0.8
density	0.122 ± 0.001	0.097 ± 0.002	0.101 ± <0.001	0.115 ± 0.001	0.116 ± <0.001
M/d	30.9 ± 4.7	32.6 ± 2.3	40.4 ± 6.2	11.6 ± 1.6	25.2 ± 6.5

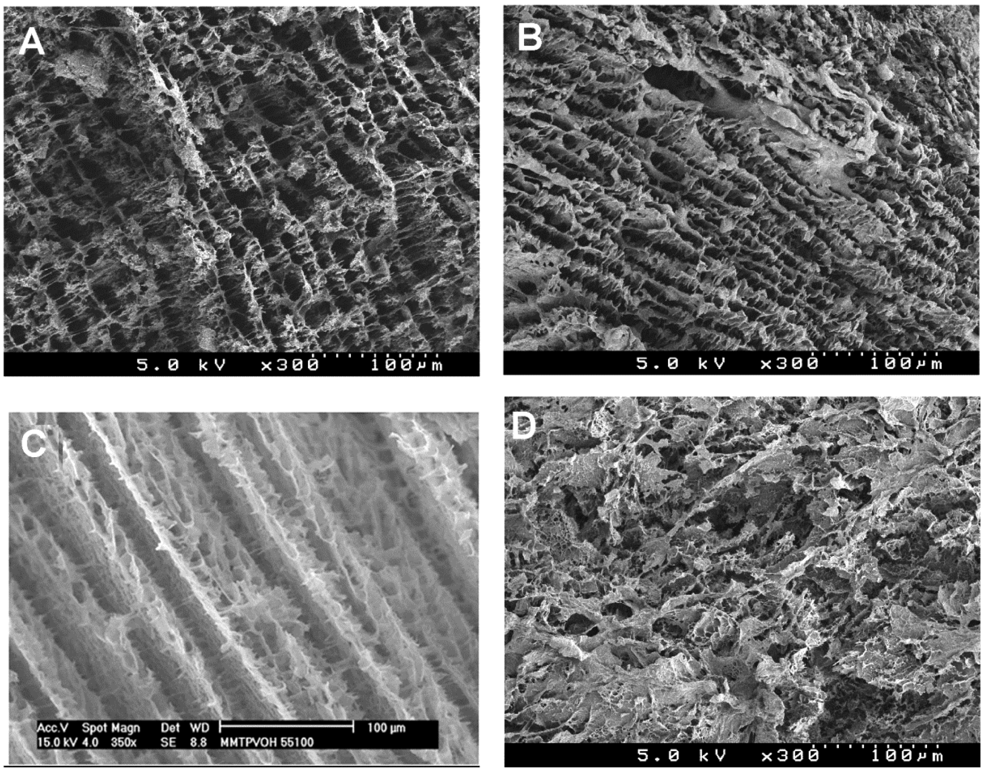

Figure 1. SEM images of aerogel composites (A) PVOH/SiO$_2$, (B) PVOH/halloysite, (C) PVOH/MMT, and (D) PVOH/laponite.

mentioned freeze-drying method. The mechanical properties, thermal stabilities, microstructures, and flammabilities will be presented, along with a proposed mechanism for modification of flammability. The choice of PVOH as the matrix polymer for this study was made based on its use in a growing body of aerogel publications, allowing previous work to be compared to compositions containing alternative filler materials, so that flammability data could be added to that body of knowledge. The current materials were not cross-linked to minimize moisture sensitivity, but such methods are known.[13,16,18]

EXPERIMENTAL SECTION

Materials. Poly(vinyl alcohol) (PVOH; M_n = 31000−50000), silicon dioxide (12 nm; Aldrich Chemical Co.), sodium montmorillonite [Na$^+$-MMT; PGW grade, cation-exchange capacity (CEC) 145 mequiv/100 g; Nanocor], laponite (CEC 60 MEQV; Southern Clay Products), and halloysite (Dragonite; Applied Minerals Inc.) were used without further purification. Deionized (DI) water was obtained using a Barnstead RoPure reverse-osmosis system. Commercial expanded polystyrene packaging foam (EPS), with a bulk density of 0.015 g/cm^3, was obtained locally as recycled packaging material and was used as a control for flammability measurements.

Aerogel Composite Fabrication. Percentages of PVOH and nanofillers are given based on aqueous mixtures prior to freeze-drying; all of the PVOH-based aerogel composites investigated in this paper were produced from aqueous mixtures that contained 5 wt % PVOH and 5 wt % inorganic nanofiller prior to freezing and sublimation.

To produce an aerogel composite containing MMT, for example, 5 g of Na$^+$-MMT was blended with 50 mL of DI water on the high speed setting of a Waring model MC2 mini laboratory blender for 1 min to obtain a 10 wt % clay aqueous suspension. A total of 5 g of PVOH was dissolved in 50 mL of DI water at 80 °C to create 10 wt % PVOH solutions. Then the aforementioned clay suspension and PVOH solution were slowly mixed together to obtain a 5 wt % MMT and 5 wt % PVOH solution. The resulting mixture was poured into polystyrene vials and immediately frozen in a solid carbon dioxide/ethanol bath (∼−80 °C). The frozen samples were dried in a VirTis Advantange freeze dryer, with an initial shelf temperature of 25 °C and a condenser temperature of −80 °C, and an ultimate 5 µbar vacuum was applied to sublime the ice.

The resultant sample was identified as PVOH/MMT. Other aerogels were fabricated according to similar procedures and noted as PVOH/laponite, PVOH/halloysite, and PVOH/SiO$_2$. Neat 10 wt % PVOH aerogel was also fabricated as a control.

Characterization. The densities of the dried aerogels were calculated from mass and dimension measurements using mass measurements and digital calipers.

Compression testing was carried out on the cylindrical specimens (∼20 mm in diameter and height) using an Instron model 5565 universal testing machine, fitted with a 5 kN load cell, at a crosshead of 10 mm/min. Five samples for each specimen were tested for reproducibility, following the ASTM D3575 method. The initial modulus was calculated from the slope of the linear portion of the stress−strain curve.

The microstructure of the aerogels was obtained with a Hitachi S-4500 scanning electron microscope at an acceleration voltage of 5 kV.

The samples were fractured in liquid nitrogen and then coated with platinum before testing.

Thermal stabilities were measured on a TGA Q500 (TA Instruments) under a nitrogen flow (40 mL/min). The samples (about 5 mg) were placed in a platinum pan and heated from ambient temperature to 600 °C at 10 °C/min.

Limiting oxygen index (LOI) values were characterized on an Oxygen Index Flammability Gauge (HC-2C) according to ASTM D 2863-97.

Cone calorimetry tests were performed according to the ISO 5660 standard with a FTT (UK) cone calorimeter. Specimens with a size of 100 mm × 100 mm × 2.5 mm, wrapped in aluminum foil, were tested under a heat flux of 50 kW/m^2. Results given in the figures that follow are exemplary curves, typical of the ±10% reproducibility typically found in such tests; the values reported are averages of three measurements.

■ RESULTS AND DISCUSSION

Fabrication of PVOH-Based Aerogels. The current study made use of the fabrication of polymer/clay aerogels via an environmentally friendly freeze-drying process that has been widely reported in recent years. Key material properties, including the density, compressive modulus, and specific modulus (ratio of the compressive modulus to the density), of the PVOH aerogels and aerogel composites are presented in Table 1. The fillers chosen for use in this study were selected in order to introduce lamellar, disklike, particulate, and fibrous reinforcement (MMT, laponite, silica, and halloysite, respectively). It can be seen that PVOH/laponite aerogels possess the highest compressive moduli among the four systems tested, 4.1 ± 0.6 MPa, which can be partially explained by their microstructure (Figure 1). All four compositions adopted layered architectures that followed the direction of ice growth, as reported previously,[10] with the exception of PVOH/laponite, which exhibited an irregular network structure, which might be caused by the retarded ice growth in a viscous solution, consistent with the high affinity of laponite for aqueous gel formation.[41] The choice of 31000−50000 D molecular weight PVOH for this study was made based on prior work, which demonstrated this range to be optimal for processing using the freeze-drying method.[10,17]

Thermal Stability. The thermal stabilities of PVOH-based aerogels were investigated by thermogravimetric analysis (TGA; Figure 2 and Table 2). Both PVOH and the nanofillers are hydrophilic and easily absorb water because of their abundant surface hydroxyl groups. The first weight loss stages observed in the TGA traces are attributed to the desorption of water, which is seen below 100 °C. The main weight loss stage, between 200 and 350 °C, is likely caused by decomposition of PVOH. Among the four composites tested, PVOH/halloysite exhibited the highest onset decomposition temperature ($T_{d,10\%}$) and the lowest char residue. The other three materials showed similar onset decomposition temperatures; PVOH/SiO_2 and PVOH/MMT left comparatively high residues. From the weight percentages of the residues, it can be concluded that they are primarily composed of nanofillers.

Combustion Behavior. The LOI values for the samples were obtained for estimating their flammabilities and are summarized in Table 3, which shows slightly increased LOI values with the addition of inorganic nanofillers. Further investigation revealed that only the sample surfaces catch fire during the LOI experiment, spreading rapidly so as to fail to meet the test. The centers of the samples were not burned during LOI testing, a result of surface burning and the low thermal conductivity of the aerogels.[41] The candlelike configuration caused by viscous melts of nanocomposites does not occur in this study,[42,43] likely because of the high filler concentration and low dripping tendency of PVOH.

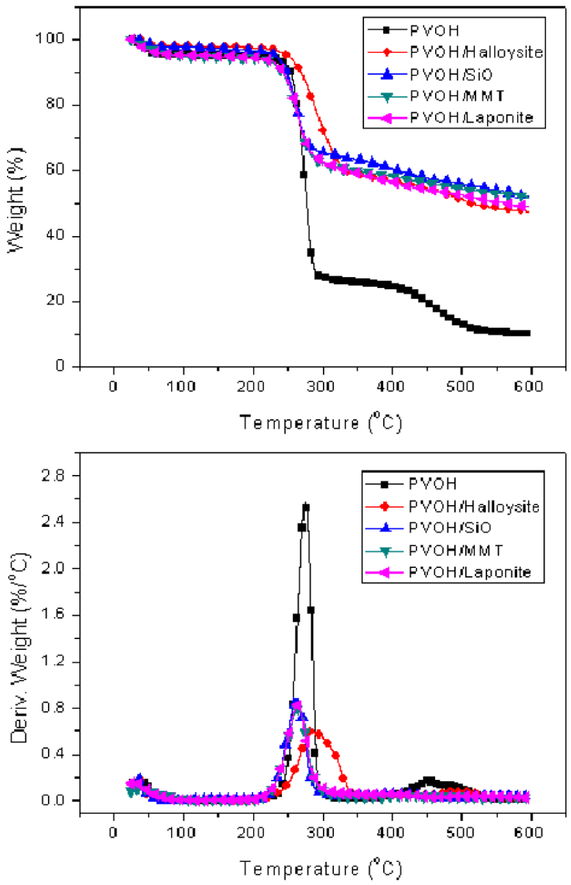

Figure 2. TGA weight loss and differential thermal gravimetry curves of PVOH-based aerogels.

Table 2. TGA Data of Freeze-Dried PVOH-Based Aerogels

sample	$T_{d,10\%}$ (°C)	$T_{d,max}$(°C)	d_W/d_T (%/°C)	residue (%)
PVOH	253.7	275.0	2.54	9.9
PVOH/MMT	242.0	265.1	0.80	51.8
PVOH/laponite	243.1	264.1	0.82	48.9
PVOH/halloysite	268.7	286.8	0.60	47.4
PVOH/SiO_2	247.9	262.8	0.87	51.9

Table 3. LOI Values of PVOH-Based Aerogels

	PVOH	PVOH/ MMT	PVOH/ laponite	PVOH/ halloysite	PVOH/ SiO_2
LOI	22.0 ± 0.5	24 ± 0.5	25 ± 0.5	24 ± 0.5	25 ± 0.5

Cone calorimetry is widely used to quantitatively evaluate the flammability in more thermodynamic terms, providing abundant information on the combustion behavior.[42−46] Parameters including the time to ignition (TTI), heat release rate (HRR), peak of heat release (pHRR), time to peak of heat release (TTPHR), total heat release (THR), specific extinction area (SEA), total smoke release (TSR), and carbon monoxide (CO) production are obtained to evaluate their flammability and toxicity. The corresponding data of neat PVOH aerogels and of EPS are also included as controls and are summarized in Table 4. Polar polymers, such as PVOH, do equilibrate with

Table 4. Burning Parameters of PVOH-Based Aerogels from a Cone Calorimeter

sample	weight (g)	TTI (s)	pHRR (kW/m^2)	TTPHRR (s)	FIGRA (W/s)	THR (MJ/m^2)	residue (%)
EPS	3.2	9	256	45	5.7	9.1	8.7
PVOH	26.3	13	378	70	5.4	52.5	1.0
PVOH/halloysite	24.9	4	121	30	4.0	23.9	45.1
PVOH/SiO_2	23.9	3	110	25	4.4	18.0	47.1
PVOH/MMT	22.5	2	108	25	4.3	14.1	62.4
PVOH/laponite	23.3	1	98.6	25	3.9	12.1	59.1

atmospheric moisture. The aerogels investigated in this study appear to absorb up to approximately 2 wt % moisture; flammability data are not adjusted for this moisture because, in actual use, such moisture would be present in the materials.

TTI refers to the time required for a sample to ignite, under the heat flux of a cone calorimeter. During cone calorimetry tests, ignition occurs when the combustible gas from a degraded polymer reaches a certain concentration.[47] The TTI values of the four aerogel composites decreased compared with that of a pure PVOH aerogel, a common phenomenon wherein TTI is usually decreased by the addition of silicates.[23] It is possible that the clay catalyzes degradation of the polymer, or this phenomenon may be a consequence of the rapid temperature increase on the surface of nanocomposites because thermal diffusion was blocked by the increased melt viscosity of such materials.[48]

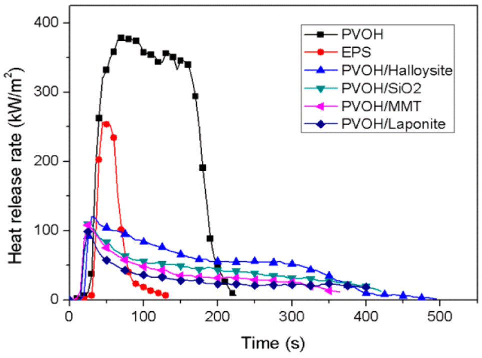

Figure 3. HRRs of aerogel samples and EPS as a function of the burning time.

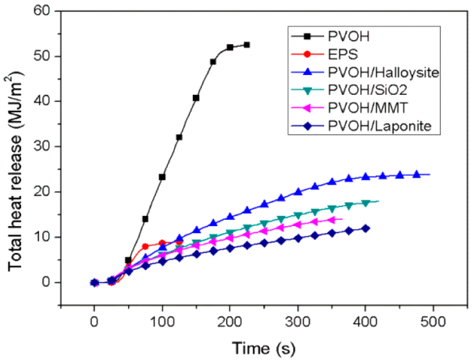

Figure 4. THRs of aerogel samples and EPS as a function of the burning time.

Figure 3 shows the HRRs of PVOH aerogel composites, PVOH aerogel, and EPS. The HRRs of all the four aerogel composites were significantly reduced compared with that of a neat PVOH aerogel, which is also much lower than that of EPS. The pHRR (Table 4) of PVOH aerogels is 378 kW/m^2, and those of PVOH aerogel composites decrease to approximately 100 kW/m^2. As a control, the pHRR of EPS is 256 kW/m^2. It should be noticed that EPS shrinks under heat flux; thus, the actual heating power on the EPS surface was lower than the setting value for further distances from the colorimeter heater; lower heat flux generally corresponds with lower pHRR.[44] PVOH/halloysite exhibited the highest pHRR among the four aerogel composites probably because of its low gas barrier and high thermal conductivity. Nanosilica is also used to reduce the polymer flammability because of its ability to increase the melt viscosity and float to the material surface when burning (because of its high surface free energy); the pHRR of PVOH/SiO_2 is lower than that of PVOH/halloysite likely because of these same behavor. The layered systems PVOH/MMT and PVOH/laponite have comparatively lower pHRR; for PVOH/laponite, the pHRR decreased to 98.6 kW/m^2 probably because of the enhanced gas barrier properties when layered silicates are added. The network structure of PVOH/laponite can further strengthen this effect. Although the pHRR values of aerogel composites were significantly decreased from the unfilled material, the TTPHRR values were obviously decreased, not a desirable phenomenon. The fire growth rate index (FIGRA) was also used to evaluate the flame spread rate, defined as the ratio of pHRR to TTPHRR, which was lower for all of the aerogel composites. THR is a very important parameter in a fully developed fire, determined by the volatile decomposition products of the material. Previous studies revealed that THR was not greatly influenced by the presence of silicates;[23,49] the THR values were significantly reduced with the introduction of nanofillers in this study. Assuming that the amounts of PVOH burnt in a neat PVOH aerogel and aerogel composites would be equal, the theoretical THR of aerogel composites should be 27.3 MJ/m^2 (ignoring any heat release from the inorganic nanofillers). As can be observed in Table 4, the THR of PVOH/halloysite decreased to 23.9 MJ/m^2 and then to 18.0 MJ/m^2 of PVOH/SiO_2, 14.1 MJ/m^2 of PVOH/MMT, and 12.1 MJ/m^2 of PVOH/laponite. Figure 4 shows that the THRs of all of the samples increased obviously at the initial burning stage and then slowly, which is in accordance with the weight loss (Figure 5). The explanation of decreased THR in composite aerogels should be combined with that for the residues (Figure 6), which shows that both pure PVOH aerogel and EPS are almost burned completely. PVOH in PVOH/halloysite composite aerogels was also almost completely consumed, with a residue of 45.1 wt %. The residue of PVOH/SiO_2 shows that it is partially burnt, with black residue and domains of the original aerogel (nanosilica is white). For layered systems, at least one-third of the samples remained after burning, with char on the surface, which means that the temperature of the sample far from the upper surface is lower than the onset degradation temperature during the cone test. This test confirmed the low

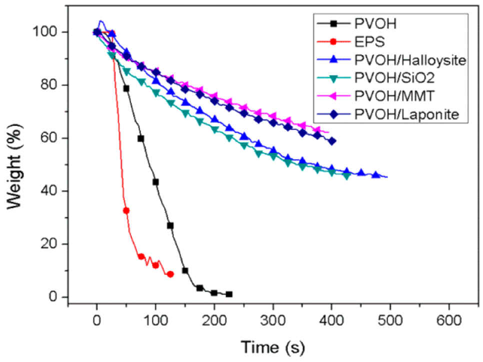

Figure 5. Weight loss of aerogel samples and EPS as a function of the burning time.

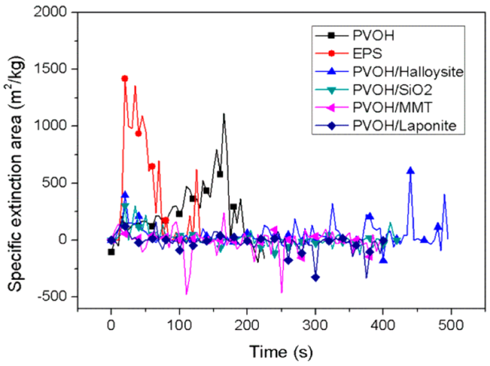

Figure 7. SEAs of aerogel samples and EPS as a function of the burning time.

thermal conductivity of aerogel composites[41] and that no shape change is observed during burning. The aforementioned properties make such polymer/clay aerogels candidates for fire-sensitive applications.

Figures 7 and 8 present the curves of SEA and TSR as a function of the burning time, respectively. It can be seen that the smoke emitted during polymer combustion was significantly decreased with the addition of nanofillers. Smoke is the incompletely combusted particles rising with the ascending gaseous products and poses an enhanced risk for suffocating. In a much lower burning rate contributed by nanofillers, aliphatic PVOH can be burned completely with little smoke. CO production was also investigated in order to figure out the toxicity of combustion products. The corresponding curves are illustrated in Figure 9. The tendency of CO production is similar to that of SEA, which obviously decreased with the addition of nanofillers. It is much lower compared with EPS; even EPS has much lower weight. Interestingly, at the last burning period of PVOH/halloysite, a huge CO production peak occurs. The speculation may be that cracking of the sample leads to incomplete burning when the combustible products burst out (Figure 6).

■ CONCLUSIONS

PVOH aerogel composites with different inorganic nanofillers, including nanosilica, halloysite, montmorillite, and laponite, were fabricated via a freeze-drying method. The compression

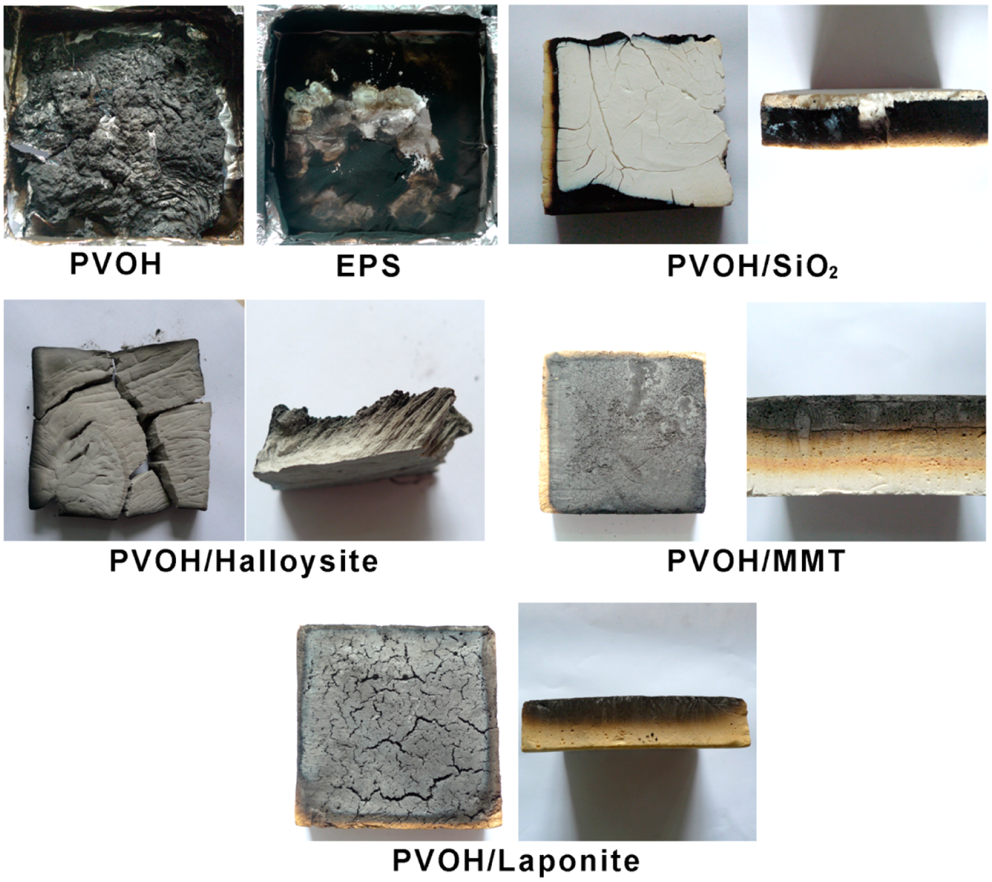

Figure 6. Residues of aerogel samples and EPS after the cone calorimetry test.

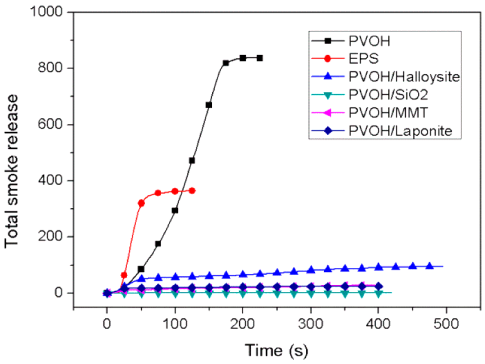

Figure 8. TSRs of aerogel samples and EPS as a function of the burning time.

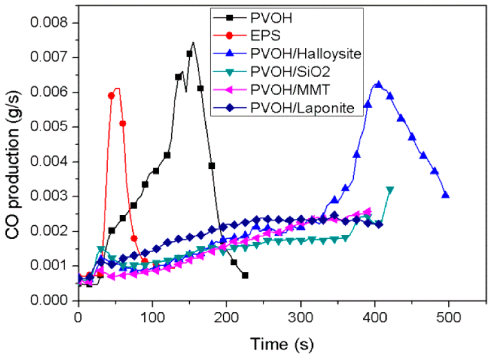

Figure 9. CO production of aerogel samples and EPS as a function of the burning time.

test shows that PVOH/MMT and PVOH/Laponite have similar compressive moduli, higher than those of PVOH/SiO_2 and PVOH/halloysite. SEM characterization revealed layered microstructures except for PVOH/laponite, which shows an irregular network morphological structure. TGA tests of aerogel samples showed increased thermal stability with the addition of nanofillers, with PVOH/halloysite exhibiting the most useful properties among the four aerogel composites. Combustion testing shows slightly increased LOI values and decreased TTI with the addition of nanofillers. HRR, THR, TSR, and CO production all decreased significantly, much lower than those for commercial EPS. Layered structure nanofillers have lower flammability than was found with spherical and fibrous nanofillers, mainly because of the enhanced barrier effects associated with layered nanofillers. This work demonstrates the feasibility of fabricating low-density materials with high flame retardancy by the addition of inorganic nanofillers. The adjustable nanofiller concentration makes them promising substitutes for polymer foams with requirements of fire safety.

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Notes

The authors declare the following competing financial interest(s): Both D.A.S. and Case Western Reserve University own small shares in Aeroclay llc (Austin, TX), which is commercializing the CWRU-developed aerogel products.

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This paper was published on the Web on April 22, 2014. The third affiliation was moved to the back of the paper as the present address for Hong-Bing Chen, and the corrected version was reposted on April 25, 2014. Due to a production error, the affiliations were incorrect. The corrected version was reposted on May 5, 2014.