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Effects of Molecular Weight upon Irradiation-Cross-Linked Poly(vinyl alcohol)/Clay Aerogel Properties

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ABSTRACT: Facile fabrication of mechanically strong poly(vinyl alcohol) (PVOH)/clay aerogel composites through a combination of increasing polymer molecular weights and gamma irradiation-cross-linking is reported herein. The aerogels produced from high polymer molecular weights exhibit significantly increased compressive moduli, similar to the effect of irradiation-induced cross-linking. The required irradiation dose for fabricating strong PVOH composite aerogels with dense microstructure decreased with increasing polymer molecular weight. Neither thermal stability nor flammability was significantly changed by altering the polymer molecular weight or by modest gamma irradiation, but they were highly dependent upon the polymer/clay ratio in the aerogel. Optimization of the mechanical, thermal, and flammability properties of these composite aerogels could therefore be obtained by using relatively low levels of polymer, with very high polymer molecular weight, or lower molecular weight coupled with moderate gamma irradiation. The facile preparation of strong, low flammability aerogels is an alternative to traditional polymer foams in applications where fire safety is important.

KEYWORDS: *aerogel, poly(vinyl alcohol), molecular weight, gamma irradiation, mechanical properties*

1. INTRODUCTION

Since montmorillonite clay aerogels fabricated using a freeze-drying method were first reported by Mackenzie and Call in the 1950s,[1,2] they have drawn attention for the good thermal, absorption, and insulation properties.[3−8] Modifications of neat clay aerogels were developed to compensate for their mechanical properties, which are insufficient for practical use.[9−12] Mechanically strong polymer/clay aerogel composites have been prepared through solution blending,[6,13−22] but at the cost of reduced thermal stability and increased flammability compared to the clay-only materials, thus requiring the use of minimized polymer loadings, in conflict with optimized mechanical properties.

Johnson et al. invented a bioinspired approach to mineralize an active polymer/clay aerogel composite,[23] which shows marked improvement of the mechanical properties with increasing modification. This inorganic mineralization does not increase the flammability of the material. Gawryla et al.[24] reported clay aerogel/cellulose whisker nanocomposites, in which a nanoscale "wattle and daub" (mud-like clay and straw-like cellulose whiskers) structure formed with compressive strengths significantly higher than predicted by simple additive behavior of properties of the individual components. It is speculated that the main reason for this synergy is the formation of three-dimensional network structures.

In our previous publications, it was recognized that suspensions with low viscosities present little resistance to the growth of an ice front (during a freeze-drying process), allowing for the formation of lamellar ice layers.[25−28] Growth of ice crystals is retarded in high-viscosity solution, resulting in more fractal growth and secondary crystallization of water and the generation of a greater number of structural links between the aerogel layers, which means a three-dimensional network structure. Thus, the cross-linking method, as an efficient way to increase solution viscosity, was developed in polymer/clay aerogel preparation. Pojanavaraphan et al.[29] fabricated cross-linked natural rubber clay aerogel composites using sulfur monochloride as the active agent; the mechanical properties increased 26-fold compared to control materials. The cation-cross-linked pectin/clay aerogel and alginate/clay aerogel were also prepared through a freeze-drying process, also with significantly increased mechanical properties.[27,30] Poly(vinyl alcohol) (PVOH) gels and derivative aerogels were also reported; the compressive moduli of divinylsulfone cross-linked PVOH aerogels were increased by as much as 29-fold by that chemical modification.[31] The compressive moduli of irradiation-cross-linked PVOH/clay aerogels were observed to increase by a factor of 10−12 compared to the starting materials.[28]

Many approaches to increasing polymer/clay gel viscosity prior to freeze-drying have been examined, in hopes of obtaining a denser microstructure and increased mechanical properties in the final product. Increasing the polymer molecular weight would, of course, increase solution viscosity[32−34] and, thus, could be expected to influence the aerogel morphological structure. In the present study we report

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the fabrication of poly(vinyl alcohol) (PVOH)/clay aerogels with various molecular weights, coupling with gamma irradiation-cross-linking. Gamma irradiation is known to bring about cross-linking in PVOH solutions, through a free radical process;[35] aerogels possessing good mechanical properties yet containing the relatively low PVOH levels ideal for minimized flammability could potentially be produced in this manner. The rheological properties of the solution, the morphologies, mechanical properties, and the combustion behaviors of the resulting PVOH/clay aerogel are reported herein for the first time, to the best of our knowledge.

2. EXPERIMENTAL SECTION

2.1. Materials. P3 (Poly(vinyl alcohol), Mw 31,000−50,000, 99% hydrolyzed), P8 (Poly(vinyl alcohol), Mw 89,000−98,000, 99% hydrolyzed) and P18 (Poly(vinyl alcohol), Mw 146,000−186,000, 99% hydrolyzed) were purchased from Sigma-Aldrich. Sodium Montmorillonite (Na^+-MMT; PGW grade with a cation exchange capacity of 145 mequiv/100 g) was purchased from Nanocor Inc. Deionized (DI) water was prepared using a Purelab flex 3 unit. All reagents were used without further purification.

2.2. Aerogel preparation. Percentages of PVOH and clay structural components are given as percentage of DI water. To produce an aerogel containing 5 wt % PVOH (using P3) and 5 wt % clay for example (noted as P3-5C5, where P3 stands for PVOH with molecular weight of 31,000−50,000, and C stands for clay), 5 g PVOH solid was dissolved in 50 mL DI water at 80 °C overnight by stirring. Five g Na^+-MMT was blended with 50 mL DI water at high speed (20,000 rpm) to create a clay suspension. The resulting mixture of clay suspension and PVOH solution were poured into polypropylene vials (diameter: 20 mm; height: 45 mm) or a poly(methyl methacrylate) (PMMA) mold (100 mm × 100 mm × 15 mm), then irradiated using a ^{60}Co source at the Institute of Nuclear Physics and Chemistry (Mianyang China) with a dose rate of 170 Gy/min. The P3−5C5 with required absorbed doses of 0 10, 30, and 50 kGy are coded as P3-5C5-0, P3-5C5-10, P3-5C5-30, and P3-5C5-50, respectively. The resulting hydrogels were then frozen in a liquid nitrogen bath (∼ −196 °C). The frozen samples were dried in a Beijing Sihuan LGJ-25C freeze-dryer with a shelf temperature of 25 °C, where a high vacuum (1−5 Pa) was applied to sublime the ice. The freeze dring process typically was given 3−4 days, however, the cross-linked samples or those produced with high molecular weight required 7 days to be fully dried.

2.3. Characterization. Densities of the aerogel samples were calculated by measuring the mass and dimensions using an analytical balance and a digital caliper.

The rheological properties of the PVOH/clay suspensions with various molecular weight were measured on a ARES G2 rheometer (TA Instruments) in the oscillatory shear mode with a parallel-plate fixture in air atmosphere. The complex viscosity (η), dynamic storage modulus (G'), and dynamic loss modulus (G'') were measured as functions of frequency ranging from 0.01 to 100 s^{-1} at room temperature (25 °C).

Compression testing was carried out on the cylindrical specimens (∼20 mm in diameter and height), using an SANS CMT7000 testing machine, fitted with a 500 N load cell, at a crosshead of 10 mm/min. Five samples for each composition were tested for reproducibility. The initial compressive modulus was calculated from the slope of the linear portion of the stress−strain curve.

Morphological microstructures of the aerogels were characterized with ZEISS EVO 18 special edition scanning electron microscope at acceleration voltage of 10 kV. The samples were prepared by fracturing in liquid nitrogen, and then sputter-coated with a thin gold layer before testing.

The thermal stabilities (by thermogravimetric analysis, TGA) were measured on a PerkinElmer STA6000 TGA under a nitrogen flow (40 mL/min). Approximately 3 mg of samples were placed in a platinum pan and heated from ambient temperature to 700 °C at a rate of 10 °C/min.

The combustion behaviors of various PVOH/clay aerogels were tested with FTT cone calorimeter. Specimens with a size of 100 mm × 100 mm × 15 mm were tested under a heat flux of 50 kW/m^2. The heat, smoke and volatile products release information were recorded.

3. RESULTS AND DISCUSSION

3.1. Preparation and properties of PVOH/clay aerogels with various molecular weights. PVOH/clay (molecular weight 31,000−50,000) aerogels with stable, workable structures after irradiation-induced cross-linking and freeze-drying were demonstrated in our previous study.[28] In the present work, PVOH with various molecular weights was utilized to fabricate PVOH/clay aerogels, and SEM micrographs of PVOH/clay aerogels with various molecular weights and irradiation levels are shown in Figure 1. Samples with two Na^+-MMT loadings, P5C5 and P2C8, were chosen as representatives to characterize the microstructure and property change upon dose and molecular weight change.

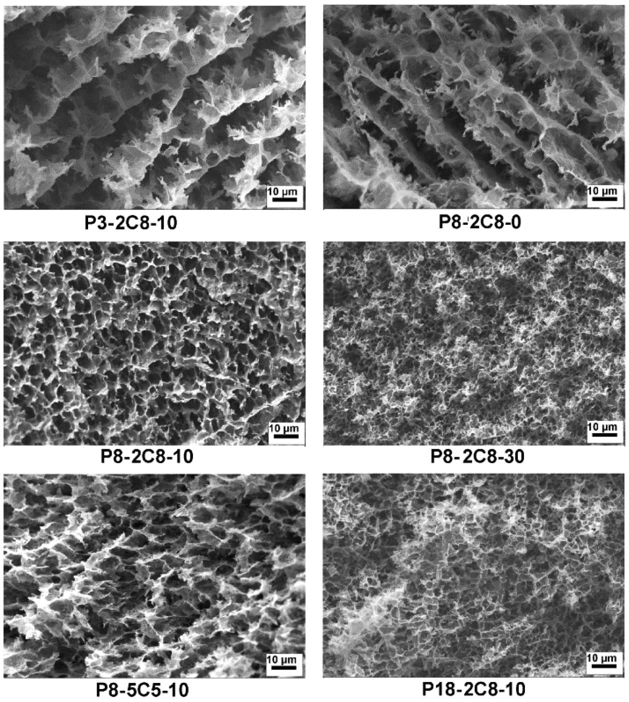

Figure 1. SEM micrographs of PVOH/clay aerogels with various molecular weights and irradiation levels.

The detailed density, compressive moduli, and specific moduli for samples with various molecular weights and irradiation doses are presented in Table 1. The data show that gamma irradiation generally increases the mechanical properties of the aerogels (indicated by their compressive moduli). For the samples containing 20% by weight PVOH, the gamma cross-linking brings about a more profound increase in modulus than is seen for the 50% PVOH series. Gamma irradiation increases moduli more significantly in aerogels produced with lower molecular weight PVOH polymers, decreasing to the point where there is little benefit to irradiation of the highest molecular weight (ca. 160 KD) polymer. The length of irradiation also influences the aerogel mechanical properties, with lower polymer molecular weight and lower polymer weight fraction aerogels benefiting from the highest levels of gamma irradiation. In every combination tested, mechanical properties were maximized with less than 50

Table 1. Mechanical Properties of PVOH/Clay Aerogels (moduli in MPa, densities in g/cm^3, specific moduli (M/d) in MPa·cm^3/g)

Sample		Property	Control	10 kGy	30 kGy	50 kGy
P3	P5C5	Modulus	4.6 ± 1.1	9.4 ± 0.3	11.4 ± 0.1	9.0 ± 2.5
		Density	0.09 ± 0	0.09 ± 0	0.09 ± 0	0.09 ± 0
		M/d	49 ± 13	112 ± 5	133 ± 5	104 ± 28
	P2C8	Modulus	1.4 ± 0.2	3.7 ± 1.1	13.2 ± 1.3	4.5 ± 2.3
		Density	0.08 ± 0.01	0.08 ± 0	0.08 ± 0	0.08 ± 0
		M/d	16 ± 2	44 ± 14	159 ± 13	55 ± 27
P8	P5C5	Modulus	9.2 ± 1.1	11.9 ± 2.0	8.6 ± 3.0	9.9 ± 4.1
		Density	0.09 ± 0.01	0.09 ± 0	0.10 ± 0	0.11 ± 0
		M/d	97 ± 11	126 ± 20	87 ± 31	88 ± 37
	P2C8	Modulus	2.0 ± 0.6	3.5 ± 0.7	5.6 ± 1.4	4.7 ± 0.7
		Density	0.09 ± 0	0.09 ± 0	0.09 ± 0.01	0.08 ± 0
		M/d	23 ± 7	41 ± 9	65 ± 13	58 ± 8
P18	P5C5	Modulus	11.1 ± 3.4	10.1 ± 3.2	5.3 ± 0.3	5.0 ± 1.9
		Density	0.10 ± 0	0.10 ± 0	0.13 ± 0.01	0.11 ± 0
		M/d	111 ± 33	107 ± 34	41 ± 5	46 ± 18
	P2C8	Modulus	4.7 ± 3.5	15.7 ± 4.1	10.2 ± 3.8	7.3 ± 4.3
		Density	0.08 ± 0	0.09 ± 0	0.09 ± 0.01	0.08 ± 0
		M/d	55 ± 40	181 ± 47	113 ± 42	91 ± 54

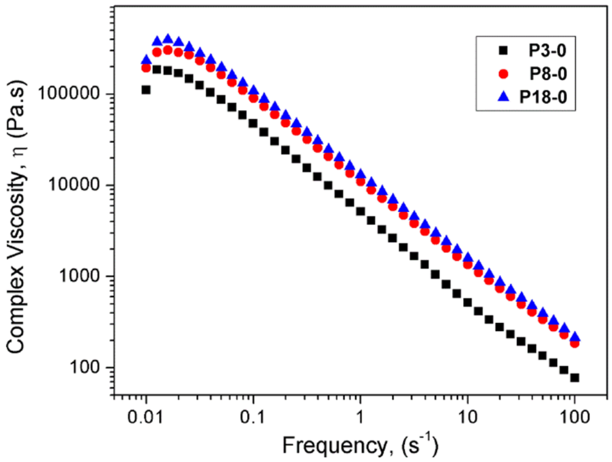

Figure 2. Angular frequency dependence of complex viscosity for PVOH/clay suspensions with various molecular weights.

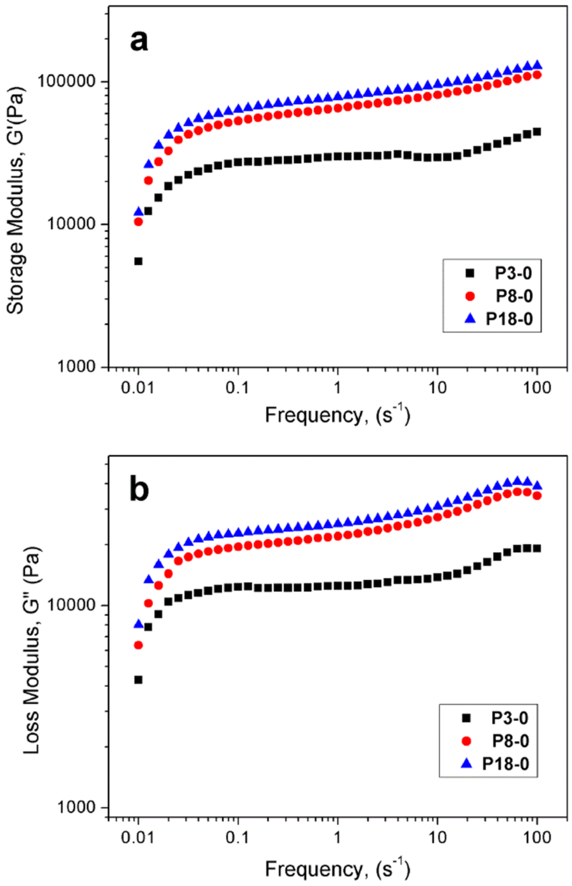

Figure 3. G' (a) and G'' (b) of PVOH/clay suspensions with various molecular weights as a function of angular frequency.

kGy of irradiation. The highest moduli and specific moduli (moduli adjusted for aerogel density) were obtained using a low concentration of the highest molecular weight PVOH, with a low dose of irradiation. Higher concentrations of the intermediate molecular weight PVOH, with a low dose of irradiation, and low and high concentrations of the lowest molecular weight PVOH with a higher dose of irradiation, gave the next highest mechanical properties within the series tested. These results show, then, that increasing polymer molecular weight tends to produce stiffer aerogels; this effect can be compensated by gamma irradiation (which in all likelihood does increase the molecular weight of the lower starting material into a critically useful range). With high molecular weight polymer, lower polymer concentrations/higher clay concentrations can be used. The combination of these two trends nicely describes the 24 materials evaluated in this study.

The aerogels show denser structures with increasing molecular weight. P3-2C8-10 shows a network structure with a pore size of about 10−20 μm; it then decreases to about 5 μm for P8-2C8-10, and finally to 1−2 μm for P18-2C8-10. The cellular structure also becomes denser with increasing absorbed dose, with cell size decreasing from about 5 μm of P8-2C8-10 to 1−2 μm of P8-2C8-30. It was noticed that the microstructure changes from a layered structure to a network structure with increasing solution viscosity. Increasing the concentration of polymer/clay in water or cross-linking the polymer are generally effective ways to increase the suspension viscosity, in accordance with denser structure.[28] Greater

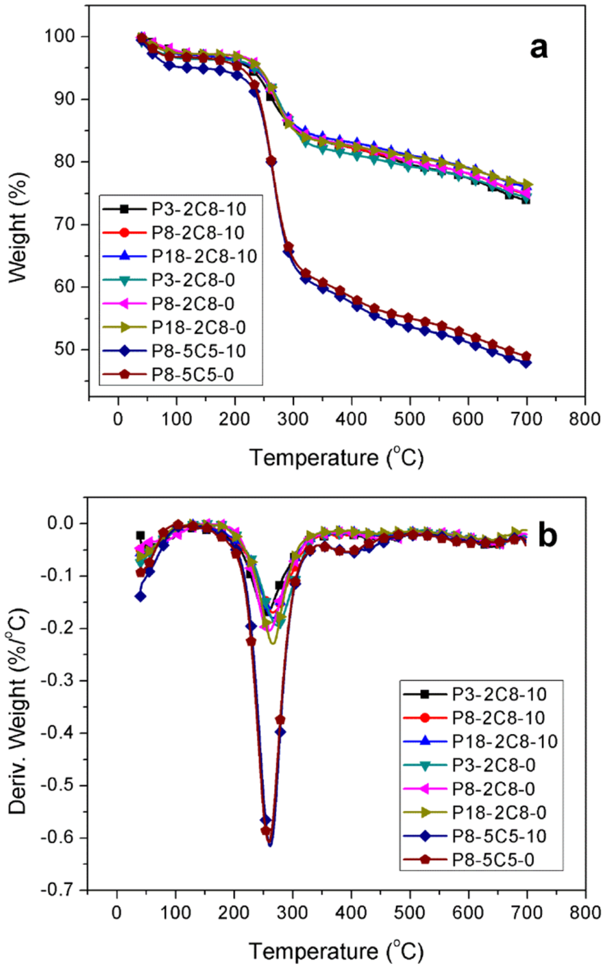

Figure 4. TGA weight loss (a) and DTG curves (b) of PVOH/clay aerogels with various molecular weights and irradiation levels.

Table 2. TGA Data of Freeze Dried PVOH/Clay Aerogels

Samples	$T_{d\ 5\%}$ (°C)	$T_{d\ 10\%}$ (°C)	$T_{d\ max}$ (°C)	d_W/d_T (%/°C)	Residue at 700 °C (%)
P3-2C8-0	234	273	275	0.19	74.3
P8-2C8-0	242	270	262	0.2	74.9
P18-2C8-0	242	271	267	0.23	76.4
P3-2C8-10	225	264	256	0.17	73.8
P8-2C8-10	231	270	261	0.17	74.8
P18-2C8-10	232	270	266	0.18	75.9
P8-5C5-0	210	242	260	0.61	48.8
P8-5C5-10	133	239	258	0.61	47.8

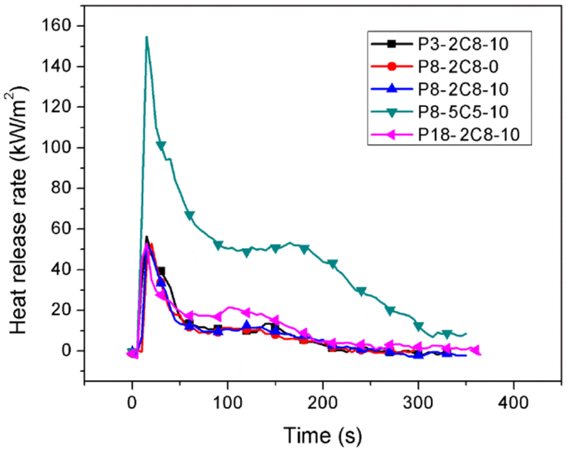

Figure 5. Heat release rate of PVOH/clay aerogels as a function of burning time.

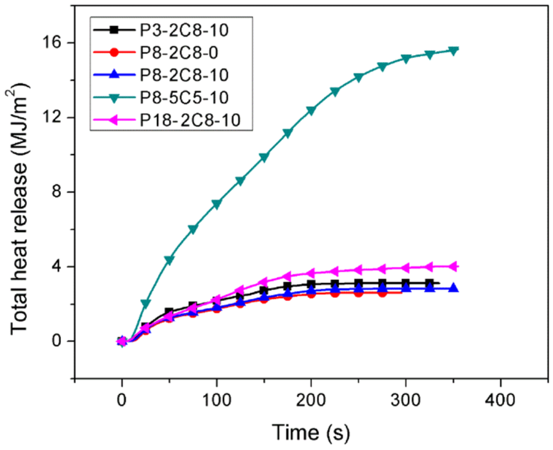

Figure 6. Total heat release of PVOH/clay aerogels as a function of burning time.

structural integrity leads to better mechanical properties. Increasing solid content would increase the densities, while probably decreasing the specific modulus; cross-linking requires additional curing. Thus, choosing polymer with suitable molecular weight is of importance.

3.2. Rheological test. The complex viscosities (η) of P5C5 solutions with various molecular weights versus angular frequency are shown in Figure 2. All three samples exhibit shear-thickening behaviors at low frequency (0.02 s^{-1}); however, shear thinning occurs with increasing frequencies. The samples produced with higher molecular weights have higher complex viscosities, demonstrating that denser gel microstructures originate from the more viscous solutions.

Figure 3 presents the angular frequency dependences of storage modulus (G') and loss modulus (G'') for PVOH/clay suspensions with various molecular weights. The G' and G'' of the three samples show a similar trend with increasing frequency, which increases with increasing molecular weight. The rheological testing results show that PVOH with higher

Table 3. Burning Parameters of PVOH/Clay Aerogels

Sample	TTI (s)	PHRR (kW/m^2)	Mean HRR (kW/m^2)	TTPHRR (s)	THR (MJ/m^2)	FIGRA (W/s)	TSR (m^2/m^2)	Residue (%)
P3-2C8-10	3	56.3	9.2	15	3.1	3.8	2.2	85.3
P8-2C8-0	7	52.7	9.0	20	2.6	2.6	21.2	84.7
P8-2C8-10	5	52.4	7.5	15	2.8	3.5	126.7	85.4
P8-5C5-10	3	154.7	28.3	15	17.1	10.3	499.0	55.6
P18-2C8-10	3	52.9	10.7	15	3.9	3.5	76.1	86.3

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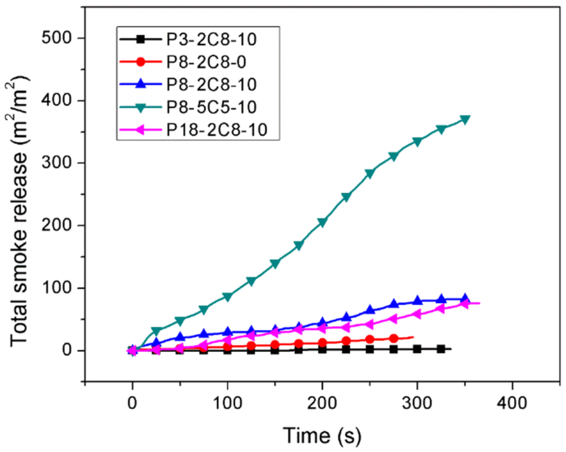

Figure 7. Total smoke release of PVOH/clay aerogels as a function of burning time.

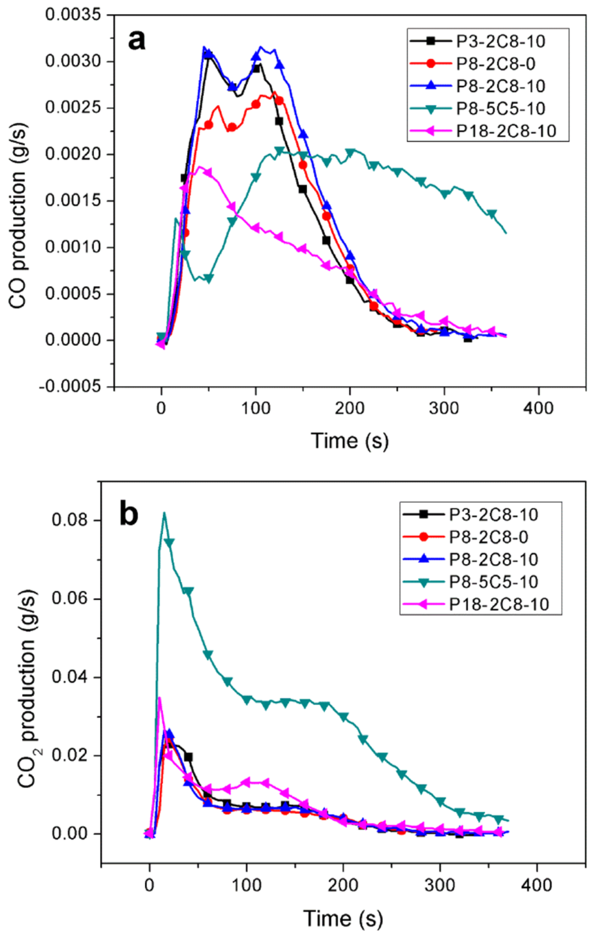

Figure 8. Release rates of main volatile products of PVOH/clay aerogels as a function of burning time: (a) carbon monoxide; (b) carbon dioxide.

molecular weight possesses higher solution viscosity, thus leading to a denser morphological structure and higher compressive moduli.

3.3. Thermal stability. The thermal stabilities of PVOH/clay aerogels produced with various molecular weight polymers were investigated by TGA (Figure 4 and Table 2). The first weight loss stage under 100 °C is likely caused by the desorption of water, $T_{d\ 2\%}$, which shows no dependence on molecular weight, but increased with increasing clay content. The absorbed dose of γ radiation did not have an obvious impact upon the desorption of water.[28] The second weight loss step is associated with the decomposition of PVOH, and $T_{d\ 10\%}$ was recorded as the onset decomposition temperature. It was previously reported that the onset decomposition temperature of PVOH/clay aerogels decreased with increasing absorbed gamma irradiation doses.[28] In the current study, little to no change in the second decomposition temperature was observed with irradiation, and char yields correspond to the clay levels, rather than polymer molecular weight or length of irradiation.

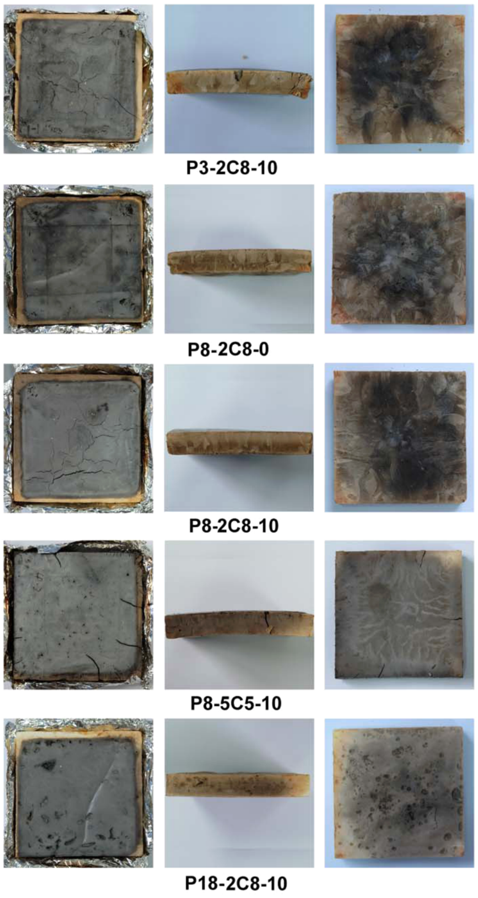

Figure 9. Photos of PVOH/clay aerogel residues after burning in a cone calorimeter; left, top; right, bottom.

3.4. Combustion behavior. PVOH/clay aerogels produced with low polymer loadings have been previously shown to possess extremely low levels of flammability.[20,28] The flammability of PVOH/clay aerogels produced with various molecular weights was determined using cone calorimetry in the present work. The corresponding data, such as time to ignition (TTI), peak of heat release rate (PHRR), mean PHRR, total heat release (THR), time to peak of heat release rate (TTPHRR), total smoke release (TSR), and fire growth rate (FIGRA), are summarized in Table 3. For samples containing 20 wt % polymer/80% clay, neither the polymer molecular weight nor irradiation with 10 kGy had any appreciable impact upon peak heat release (Figure 5) or total heat release (Figure 6). All of these 20% polymer samples showed substantially lower flammability than the 50% polymer sample tested. The smoke levels (Figure 7) observed were highly variable, and it is difficult to conclude much about the effects of molecular weight or irradiation on this variable. The CO and CO_2 levels associated with the burning of aerogels in a cone calorimeter did show little influence of polymer molecular weight, nor of gamma irradiation (Figure 8). Figure 9 shows that the shape of all the samples remains unchanged after burning, with only disconnected cracks. It is likely that the high clay loading caused some ceramic transformation during burning.[19] The newly formed network structure acts as heat and substance barrier, decreasing the fire spreading rate.

4. CONCLUSIONS

Poly(vinyl alcohol)/clay aerogel composites with various molecular weight were fabricated using an environmentally friendly freeze-drying process. The aerogels produced from high polymer molecular weights exhibit significantly increased compressive moduli, similar to the effect of irradiation-induced cross-linking. The required irradiation dose for fabricating strong PVOH composite aerogels with dense microstructures decreased with increasing polymer molecular weight. Neither thermal stability nor flammability was significantly changed by altering the polymer molecular weight or by modest gamma irradiation, but both were highly dependent upon the polymer/clay ratio in the aerogel. Optimization of the mechanical, thermal, and flammability properties of these composite aerogels could therefore be obtained by using relatively low levels of polymer, either with very high polymer molecular weight or with lower polymer molecular weight coupled with moderate gamma irradiation. Previous work has shown that polymer solubility decreases with irradiation, so if stability in the presence of water is also an important criterion, use of lower molecular weight polymer combined with gamma irradiation may lead to a globally optimized product.

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Notes

The authors declare the following competing financial interest(s): D.A.S. and CWRU have small equity positions in a startup company that conceivably could benefit from this work.

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