Comparison of Thermal Decomposition of Polystyrene Products vs. Bio-Based Polymer Aerogels

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ABSTRACT. Samples of polystyrene (PS), extended polystyrene foam (EPS foam), and 3 bio-based foam-like polymer/clay aerogels were produced, and examined under pyrolysis conditions. The polystyrene products produced pyrolysis products including toluene, styrene, benzaldehyde, and 4-phenyl-1-butyne; all consistent with previous reports. These highly flammable volatiles would be further expected to combust under flame conditions, producing carbon monoxide and carbon dioxide; prior work suggests that carbon monoxide poses the greatest health risk from the burning of both polystyrene and EPS. Pectin and alginate carbohydrate polymer aerogels, subjected to the same pyrolysis conditions as the polystyrene materials, produced products which were generally consistent with prior literature, and presented only moderate known health risks (similar to those of the EPS pyrolysis). As with PS and EPS foams, the alginate and pectin aerogel by-products are flammable, and are expected to be converted to carbon oxides. Casein, a milk-derived protein, generated organic nitriles and aromatic compounds under pyrolysis conditions, again consistent with literature for proteins in general. While none of the bio-based pyrolysis products of this study pose known significant health risks, it is possible that some of nitriles could be converted to hydrogen cyanide, leading to the recommendation that such protein-based products be further investigated prior to implementation in consumer/civil engineering applications.

INTRODUCTION

Polymer foams find applications in a wide range of products, including food and consumer product packaging, transportation, and construction (Ruiz-Herrero and Rodríguez-Perez 2015). The vast majority of these foams, most typically produced by expansion of polyethylene, polystyrene, or polyurethane, are petrochemically-derived, and consequently some of them are highly flammable. An example of such a foam product is extended polystyrene (EPS) produced from benzene and ethylene, then foamed to reduce its density from 1.04 g/cm³ to approximately 0.02 to 0.05 g/cm³ (Zarr and Pintar 2012). Because this foam is primarily air on a volume basis, its thermal conductivity similarly mirrors that of air (a typical value for EPS might be 0.033 W/(mK) vs. that for air of 0.025 W/(mK)) (Zarr and Pintar 2012).

Polymer aerogels have been proposed as replacements for polymer foams in a range of applications (Somlai et al. 2006; Pojanavaraphan et al. 2010; Wang and Schiraldi 2013; Chen et al. 2012; Shang et al. 2016;

Chen et al. 2013). These materials, most commonly produced by freeze drying of aqueous dispersions of smectite clays and polymers, or by supercritical drying of polymer gels in organic solvents, possess densities in the 0.05 to 0.15 g/cm³ range, have EPS-like thermal conductivities, and can be produced from a wide range of polymers (Schiraldi 2015). Especially interesting are polymer aerogels produced from bio-based polymers, converted to aerogels via the freeze-drying process; allowing the combination of a renewable material with a very low environmental impact process (the only effluent from the freeze-drying route to aerogels is typically just water vapor). Surprisingly, and unlike EPS and most other commercial foam materials, many of the bio-based polymer aerogels exhibit extremely low flammabilities (Chen et al. 2012; Shang et al. 2016). Not established to date is whether typical bio-based polymer aerogels release toxic gases upon combustion; both low flammability and low-smoke toxicity are necessary for many foam-replacement applications. Wool is a good example of a bio-base polymer which releases a highly toxic combustion product, in this case HCN gas (Beyler and Hirschler 2002). In order for the bio-based polymer aerogels

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to truly represent environmental improvements over EPS foam, the question of their combustion products needs to be answered. The present work examines the combustion products of a series of bio-based polymer aerogels, comparing these results with the products of EPS combustion.

MATERIALS AND METHODS
Materials

Casein, pectin, ammonium alginate, and sodium hydroxide (all Fisher Scientific), sodium montmorillonite (Na+-MMT; PGW grade, cation exchange capacity of 145 meq/100 g; Nanocor Inc.), extended EPS foam (FOAMULAR® 150, Owens Corning), and Cellofoam® (Cellofoam North America Inc.) were all used as received. Deionized (DI) water was obtained using a Barnstead|Thermolyne ROpure® reverse osmosis system. Finished polymer resins, foams, and aerogels tested in this study are given in Table 1; densities are ±5% of the values given. The commercial product compositions are as given by the manufacturers' data sheets.

Aerogel Preparation

Polymer/clay aerogels were produced from casein (milk protein) (Wang and Schiraldi 2013), alginate (derived from seaweed) (Chen et al. 2012), and pectin (a gelling fruit-based carbohydrate) (Chen et al. 2013); detailed preparations can be found in the cited references. In each case, separate mixtures of polymer and inorganic fillers-clay were produced by high shear blending, then the polymer and fillers mixtures were combined under low shear blending. The aqueous mixtures were transferred to 2 cm diameter cylindrical polystyrene vials and immediately frozen in a solid carbon dioxide/ethanol bath (~-80 °C) before being placed in a VirTis Advantage EL-85 lyophilizer for 4 days, where high vacuum was applied to sublime the ice.

Analytical Methods

Thermogravimetric analyses (TGA) were carried out using a TA Instruments Q500, operating under nitrogen and under air environments, with a 10 °C temperature ramp rate. Pyrolysis GC-MS was carried out in air at the University of Dayton Research Institute, using a CDS Analytical Model 2000 Pyroprobe equipped with a Carbolite TZF 12/38/400 furnace, connected to an HP5890/5970 GC-MS (Agilent), and total ion methodology (sample heated at 100°/min to 1000 °C).

RESULTS AND DISCUSSION

Two different extended polystyrene polymers used as commercial insulating materials, and three polymer/clay aerogels produced using casein, alginate, and pectin as the biopolymer matrixes, were characterized and subjected to TGA and pyrolysis GC/MS analysis. This testing provided a better understand of each materials' decomposition under air and under nitrogen, and determined the decomposition gases which were produced by these materials at elevated temperature. Descriptions of the materials tested are given in Table 1.

Test materials were subjected to thermal degradation conditions under both air and nitrogen

Table 1
Materials evaluated

Materials	Composition	Density (g/cm³)
Polystyrene pellets (Aldrich)	Polystyrene	1.05
Extended polystyrene insulation pink (FOAMULAR® 150)	Polystyrene 80-90% wt., 1-chloro-1-1-difluoroethane 7-12% wt., hexabromocyclododecane 0.5-1.5% wt., talc 0-2% wt.	0.021
Extended polystyrene insulation white (Cellofoam®)	Polystyrene foam 95-100% wt., pentanes (n-pentane, isopentane & cyclopentane) ≤ 2% wt.	0.015
Pectin	50% pectin, 50% Na+-MMT.	0.10
Casein	50% casein, 50% Na+-MMT.	0.11
Alginate	72% alginate, 28% Na+-MMT.	0.075

Table 2
TGA of the subject materials

Polymer [trademark name] (% filler)	Environment	Onset degradation temperature °C	Degradation range °C	Weight loss %	Residual weight %
EPS white	Air	325	325-425	100	0
[Cellofoam®]	Nitrogen	375	375-450	100	0
EPS pink	Air	325	325-425	100	0
[FOAMULAR® 150]	Nitrogen	375	375-450	100	0
Polystyrene	Air	325	325-425	100	0
	Nitrogen	375	375-450	100	0
Casein aerogel (50)	Air	50	50-100	10	
			100-200	5	50
			200-250	15	
			250-800	20	
	Nitrogen	50	50-100	10	
			200-400	40	45
			>400	5	
Alginate aerogel (28)	Air	450	450-500	85	5
			500-550	10	
	Nitrogen	375	375-475	95	5
Pectin aerogel (50)	Air	40	40-200	12	
			200-450	33	47
			450-585	8	
	Nitrogen	40	40-250	10	52
			250-800	38	

atmospheres, with rate losses characterized by TGA (Table 2). Both commercial polystyrene samples showed degradation onset temperatures of 325° and 375 °C, under air and nitrogen atmospheres, respectively, consistent with prior literature reports; all of the polystyrene samples fully degraded, with no residual material left by 500 °C (Figs. 1 to 4). The casein, pectin, and alginate aerogels exhibited more complex decomposition behaviors than seen for polystyrene, with multiple weight loss steps observed, but ultimately with nearly all of the organic matter consumed by 500 °C under air, and 800 °C under nitrogen atmosphere. The observed behaviors of alginate (Figs. 5, 6) and casein (Figs. 7, 8) mirror previously-reported TGA results (Kong et al. 2009, Moldoveanu et al. 2013). Residual weights of the aerogels—with the exception of alginate—closely mirrored the weight percentage

of the montmorillonite clay filler in the samples. Montmorillonite clay is known to be thermally stable, and is converted into a ceramic material under natural gas fire conditions present in cone calorimetry testing (Chen et al. 2012). For pectin, degradation started at 40 °C under both air and nitrogen atmospheres (Figs. 9, 10). The sample resisted complete degradation under nitrogen atmosphere until 800 °C, losing 48% of the original weight.

Decomposition products identified using total ion chromatography, with 100% gasification, are given in Table 3. The polystyrene pellets and both commercial EPS foams gave similar decomposition products: styrene, toluene, benzaldehyde, 4-phenyl-1-butyne, and 2-nitropropylbenzene; all but the latter being readily rationalized from the starting polymer structure (Figs. 11, 12). Previous workers have
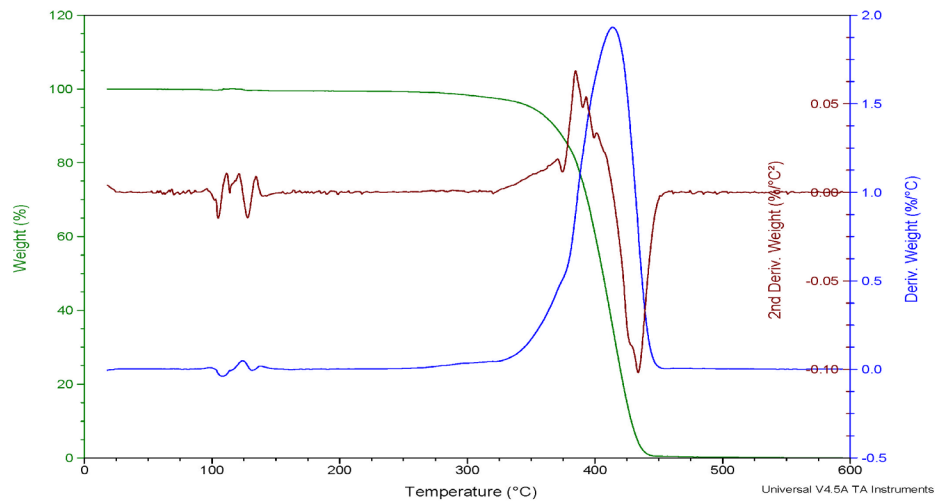
FIGURE 1. Thermogravimetric degradation analysis of extended polystyrene insulation (pink) in air
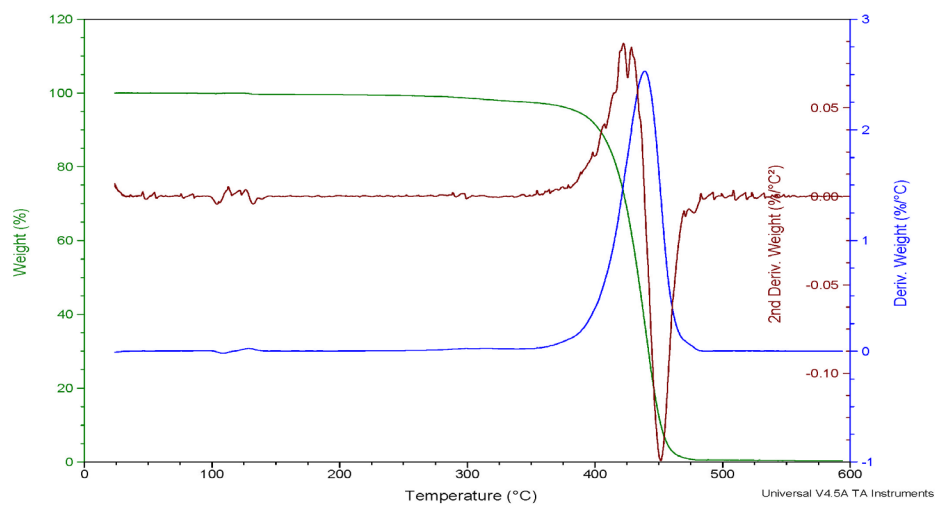
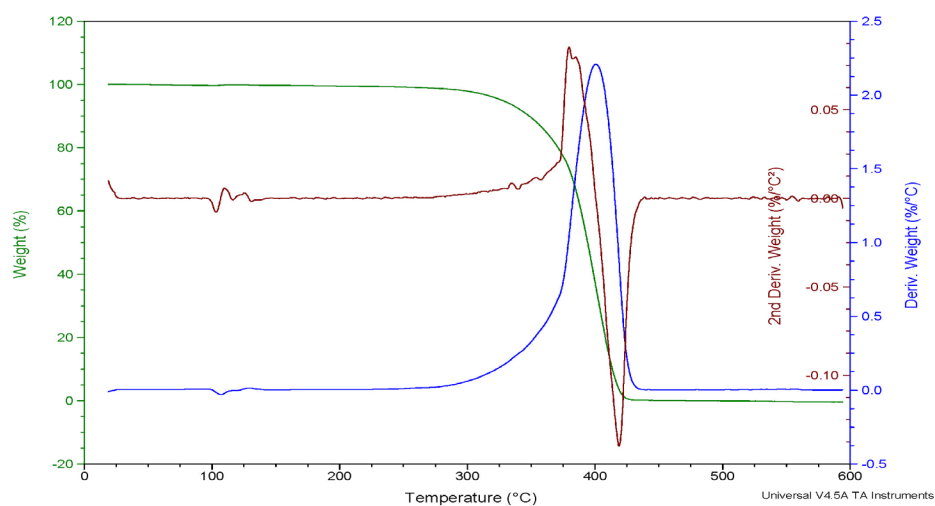**FIGURE 2.** Thermogravimetric degradation analysis of extended polystyrene insulation (pink) in nitrogen

FIGURE 3. Thermogravimetric degradation analysis of extended polystyrene insulation (white) in air
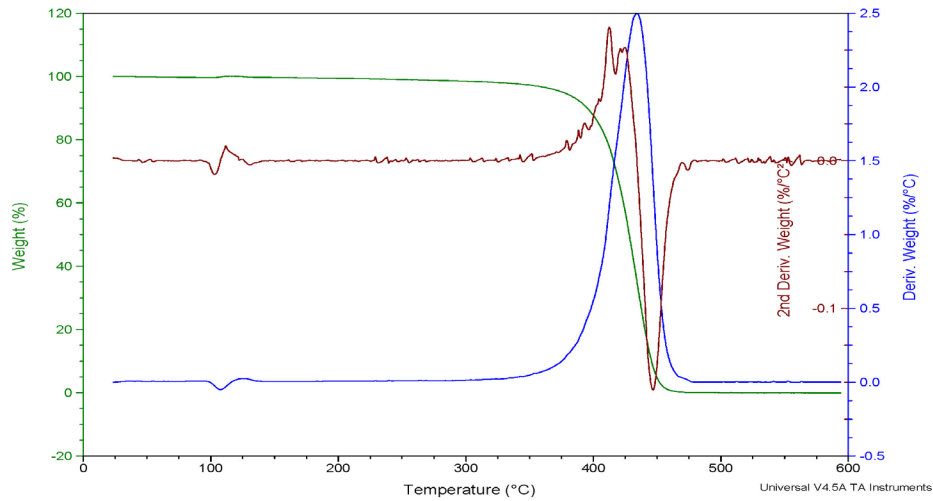
FIGURE 4. Thermogravimetric degradation analysis of extended polystyrene insulation (white) in nitrogen
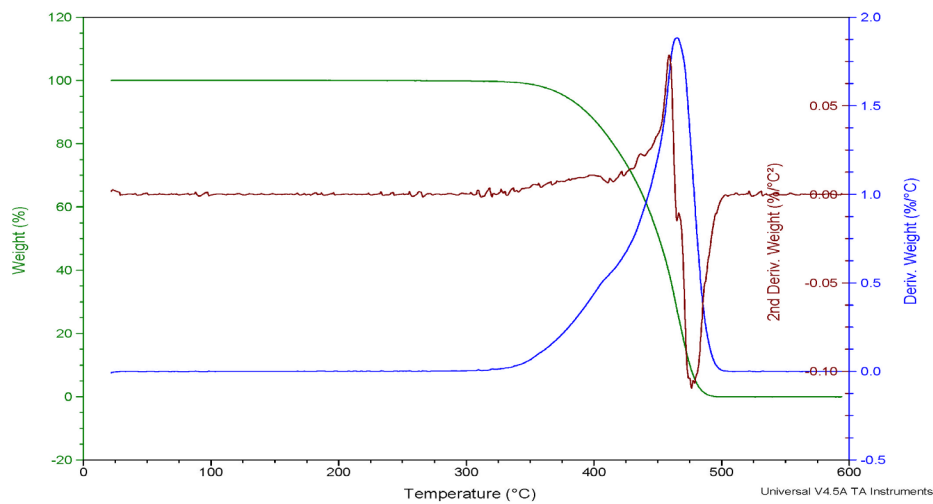
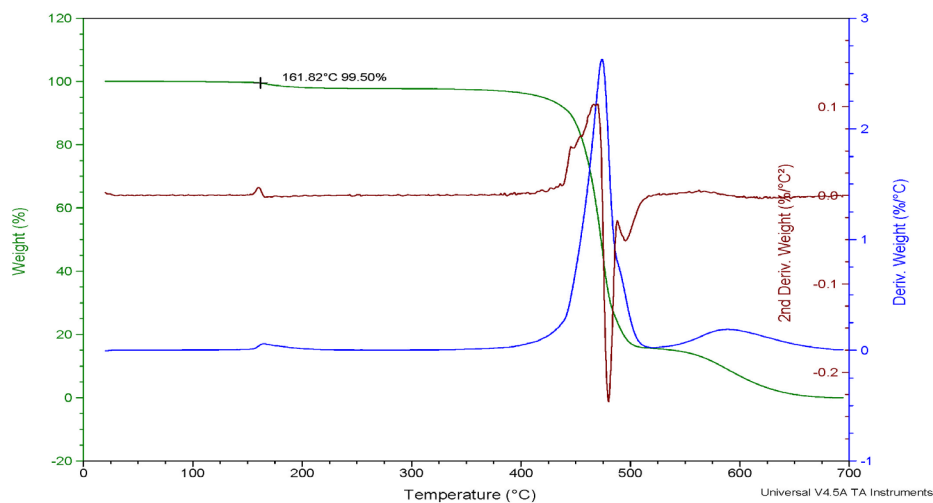**FIGURE 5.** Thermogravimetric degradation analysis of alginate in nitrogen

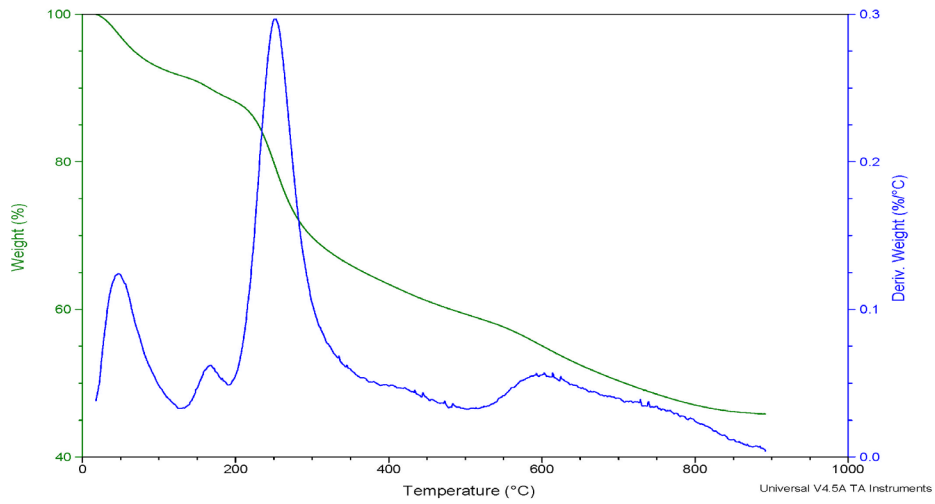**FIGURE 6.** Thermogravimetric degradation analysis of alginate in air

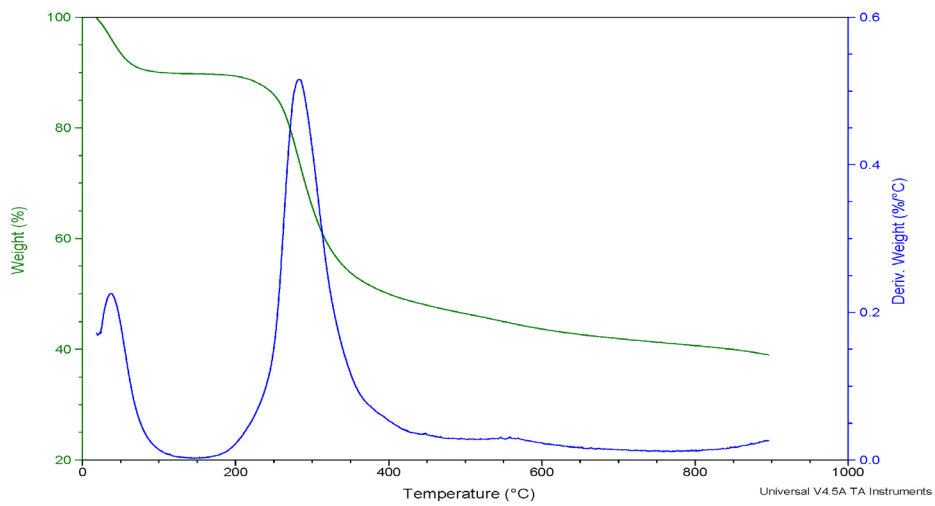**FIGURE 7.** Thermogravimetric degradation analysis of casein in air

FIGURE 8. Thermogravimetric degradation analysis of casein in nitrogen
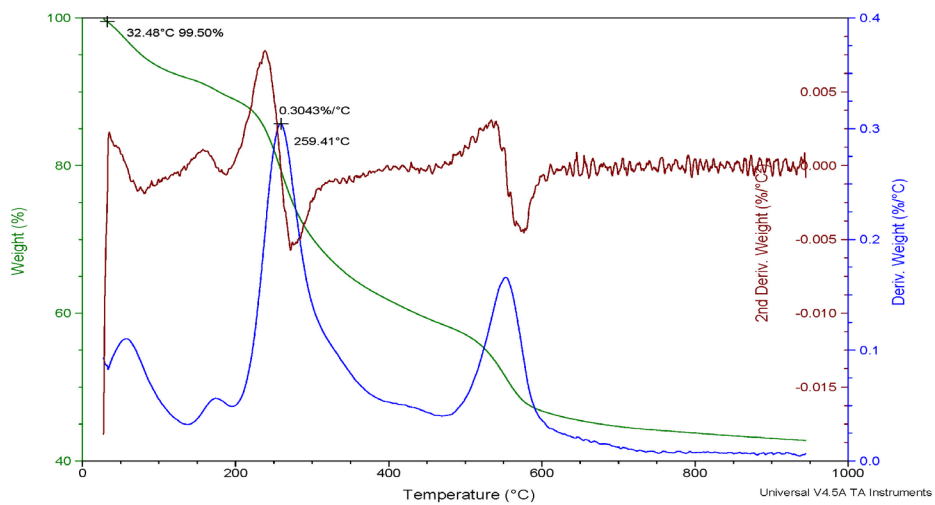

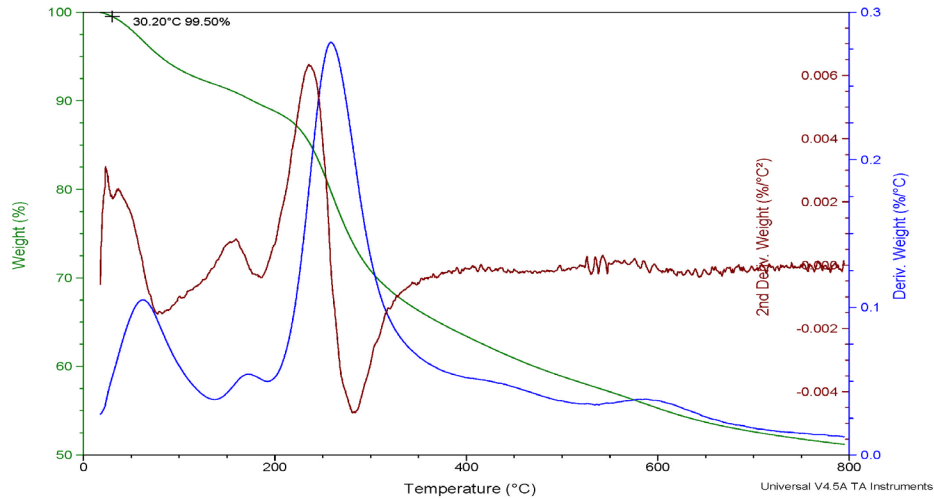**FIGURE 9.** Thermogravimetric degradation analysis of pectin in air

FIGURE 10. Thermogravimetric degradation analysis of pectin in nitrogen

Table 3
Gasified decomposition products

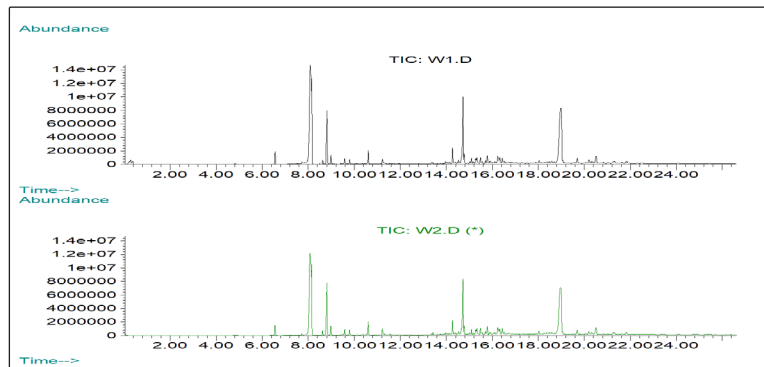| Polymers	Products detected
Polystyrene	Toluene, styrene, benzaldehyde, 4-phenyl-1-butyne, 2-nitropropylbenzene.
EPS	Toluene, styrene, benzaldehyde, 4-phenyl-1-butyne, 2-nitropropylbenzene.
Pectin	Furfural
Alginate	Undecane, dodecane, styrene, benzene.
Casein	2-nitropropane, toluene, 4-methyl-pentanenitrile, ethylbenzene, benzonitrile.

FIGURE 11. Pyrolysis GC-MS for extended commercial polystyrene insulator (white) with 222 mL/min. flow rate. Top: run 1, bottom: run 2.
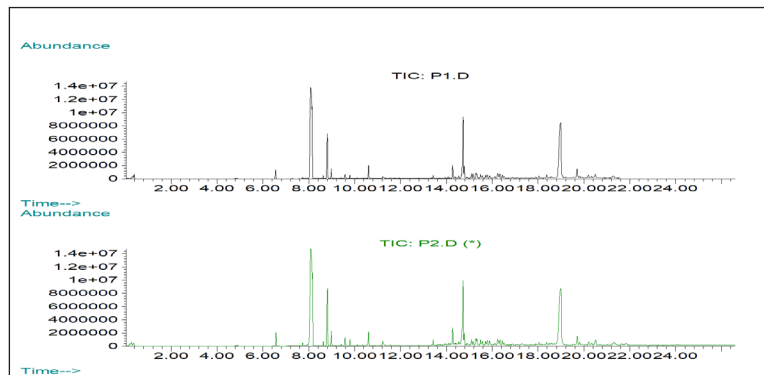

FIGURE 12. Pyrolysis GC-MS for commercial polystyrene insulator (pink) with 222 mL/min. flow rate. Top: run 1, bottom: run 2.

reported that, depending on conditions, the major decomposition products of polystyrene are styrene and benzaldehyde (Beyler and Hirschler 2002), and possibly also phenyl ethanol, styrene oxide, cumene, and acetophenone (Pfäffli et al. 1978). A full review of decomposition products is given in Gurman et al. (1987), which showed the styrene concentrations plus the decomposition gases is significantly impacted by pyrolysis temperature. A review of prior polystyrene degradation/combustion literature data reiterated the range of thermal decomposition products possible, but makes the important point that these by-products are themselves highly flammable. Hence, the major toxicity issue associated with flaming decomposition of this polymer is likely due to carbon monoxide, which is produced in high levels, along with carbon dioxide (Gurman et al. 1987). Under non-flaming conditions, when the range of organic by-products are observed, the toxicity of polystyrene by-products are much lower.

Pectin, depending on conditions, has been previously shown to generate aldehydes, such as formaldehyde, acetaldehyde, acetone, acrolein, propionaldehyde, crotonaldehyde, methyl ethyl ketone, and butyraldehyde (Zhou et al. 2011). In our study, a different aldehyde, furfural, was the volatile component that was detected (Fig. 13). While pectin, a carbohydrate, does not contain the furan moiety

present in furfural, it is not difficult to imagine a series of dehydration and decarboxylation reactions which could lead to this product. Furfural is widely known to be a pyrolysis product of lignocellulosic feedstocks, such as rice and oat husks (Gallo et al. 2013).

Alginate, also a carbohydrate, showed consistently small amounts of undecane and dodecane released upon degradation (Fig. 14). In a repeat pyrolysis, styrene and benzene were also observed. While these hydrocarbons were repeatable, it is not obvious how they could be produced from alginate, leading us to suspect that this is an artifact of the column/test method used. No other volatile products were observed from alginate degradation. Flammability studies of alginate aerogels have shown them to be among the least flammable foam-like materials known, a fact inconsistent with hydrocarbon by-products, and more consistent with a near absence of flammable gases (Chen et al. 2012; Shang et al. 2016).

Casein pyrolysis was found to produce 2-nitropropane, toluene, 4-methyl-pentanenitrile, ethylbenzene, and benzonitrile (Fig. 15), which are different from the carbon monoxide, carbon dioxide, water, ammonia, and isocyanic acid products previously reported using FTIR of thermally-degraded polymer (Moldoveanu et al. 2013). Toluene and a number of nitriles, including those detected in this study, have been
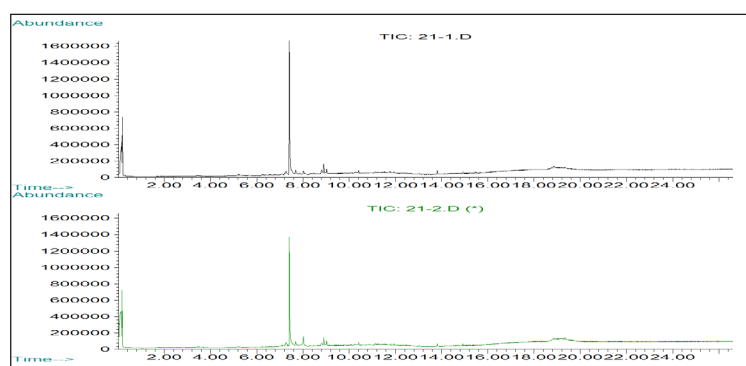

FIGURE 13. Pyrolysis GC-MS for pectin aerogel with 222 mL/min. flow rate. Top: run 1, bottom: run 2.
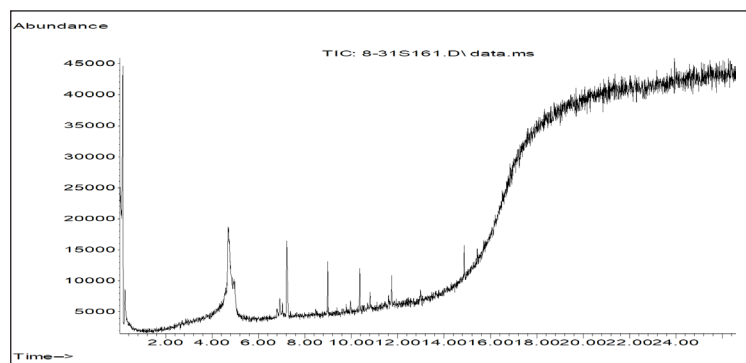

FIGURE 14. Pyrolysis GC-MS for alginate aerogel with 222 mL/min. flow rate
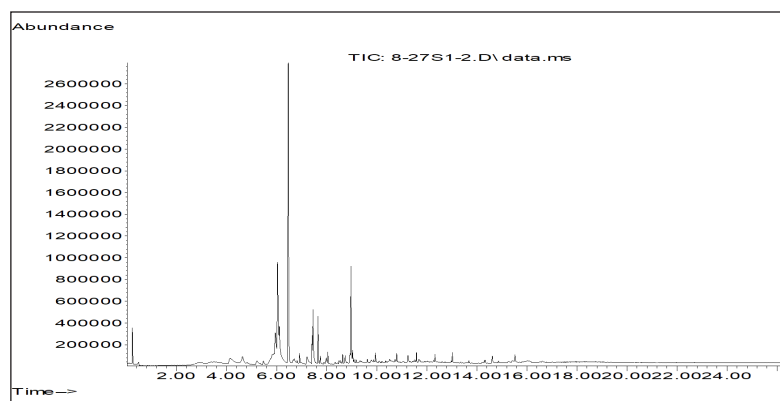
FIGURE 15. Pyrolysis GC-MS for casein aerogel with 222 mL/min. flow rate

Table 4
Published toxicities of decomposition products

Chemical byproduct	Original polymer	CAS-No	Carcinogen	Health hazards*
Undecane	Aliginate	1120-21-4	≤ 0.1 Probable/possible/confirmed in humans	1[a]
Furfural	Pectin	98-01-1	≤ 0.1 Probable/possible/confirmed in humans	2[b]
Benzaldehyde	EPS	100-52-7	No data available	2[c]
Nitropropane	Casein	79-46-9	Classified. Proven for animals.	2[d]
Nitropropyl benzene	EPS	7137-54-4	≤ 0.1 Probable/possible/confirmed in humans	4[e]
Phenyl butyne	EPS	16520-62-0	No data available	2[f]
Benzene	Aliginate	71-43-2	Classified. Confirmed for humans.	2[g]
Benzonitrile	Casein	100-47-0	No data available	2[h]
Dodecane	Aliginate	112-40-3	No data available	2[i]
Ethyl benzene	Casein	100-41-4	Possible for humans	2[j]
Styrene	EPS, aliginate	100-42-5	Possible/proven for humans	2[k]
Toluene	EPS, casein	108-88-3	Not classifiable for humans	2[l]
Methyl pentanenitrile	Casein	542-54-1	≤ 0.1 Probable/possible/confirmed in humans	2[m]

*0 = minimal hazard; 1 = slight hazard; 2 = moderate hazard; 3 = serious hazard; 4 = severe hazard

[a] MSDS CAS-No 1120-21-4, Sigma-Aldrich Inc.
[b] MSDS CAS-No 98-01-1, Sigma-Aldrich Inc.
[c] MSDS CAS-No 100-52-7, ScienceLab.com Inc.
[d] MSDS CAS-No 79-46-9, ScienceLab.com Inc.
[e] MSDS CAS-No 7137-54-4, Sigma-Aldrich Inc.
[f] MSDS CAS-No 16520-62-0, Sigma-Aldrich Inc.
[g] MSDS CAS-No 71-43-2, ScienceLab.com Inc.
[h] MSDS CAS-No 100-47-0, ScienceLab.com Inc.
[i] MSDS CAS-No 112-40-3, ScienceLab.com Inc.
[j] MSDS CAS-No 100-41-4, ScienceLab.com Inc.
[k] MSDS CAS-No 100-42-5, ScienceLab.com Inc.
[l] MSDS CAS-No 108-88-3, ScienceLab.com Inc.
[m] MSDS CAS-No 542-54-1, Molbase.com

demonstrated to be significant products of protein-rich biomass pyrolysis, specifically from *C. vulgaris* algae feedstocks (Wang 2014). In the present work, toluene was the major product, detected in 25 to 40 fold excess compared to individual nitriles and ethyl benzene; these ratios were in the 5 to 10 fold excess in Wang's work, potentially reflecting differences in protein structures and/or the pyrolysis and analytical methodologies.

Published toxicological data on the by-products of polymer pyrolysis detected in the present study are presented in Table 4. Unlike the cited production of HCN from wool, none of the bio-based aerogel pyrolysis products detected herein rise beyond "moderate hazards." As mentioned above, these pyrolysis products themselves are flammable organics in the vapor phase, so while the carbon oxides are expected to be significant combustion products, it is also possible that pyrolysis to organic nitriles could still lead to the ultimate production of HCN. Hodgkin et al., for example, detected both nitriles and HCN in the products produced when wool fabrics are burned (Hodgkin et al. 1983).

Combining the current data, we find that under pyrolysis conditions both polystyrene and extended polystyrene foam degradation products are similar to those previously reported. Carbohydrate-based polymer aerogels produce gaseous by-products which are of relatively low toxicity, which in turn, when burned, could likely be expected to further combust to carbon oxides typical of organic products. Casein, the lone protein tested in aerogel form, produced pyrolysis products typical of previously-reported protein pyrolysis studies. While no highly toxic products were detected from pyrolysis of casein aerogels, it is important to point out that further combustion of nitrile by-products potentially could lead to some level of hydrogen cyanide generation, a point that would need to be further evaluated prior to commercial installation of protein-based aerogels in construction or transportation applications.

In conclusion, polystyrene and EPS foam, under pyrolysis conditions, produce by-products such as toluene, styrene, benzaldehyde, and 4-phenyl-1-butyne which are consistent with previous reports in the literature. These highly flammable volatiles would be further expected to combust under flame conditions, producing primarily carbon monoxide and carbon dioxide; prior work has suggested that carbon monoxide poses the greatest health risk from the burning of EPS foam. Pectin and alginate carbohydrate polymer aerogels, subjected to the same pyrolysis conditions as the polystyrene materials, produced products which were generally consistent with prior literature, and presented only moderate known health risks (similar to those of the EPS pyrolysis). As with EPS foam, the alginate and pectin aerogel by-products are flammable, and are expected to be converted to carbon oxides. Casein, a milk-derived protein, generated organic nitriles and aromatic compounds, again consistent with known literature for protein pyrolysis in general. While none of the casein pyrolysis products of this study pose known significant health risks, it is possible than some of the nitriles could be converted to hydrogen cyanide in a fire, leading to the recommendation that this point be further investigated prior to implementation of protein-based aerogels in consumer or civil engineering applications.

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