

# Biodegradable Pectin/Clay Aerogels

Hong-Bing Chen,<sup>†,‡</sup> Bor-Sen Chiou,<sup>§</sup> Yu-Zhong Wang,<sup>†</sup> and David A. Schiraldi<sup>\*,‡</sup>

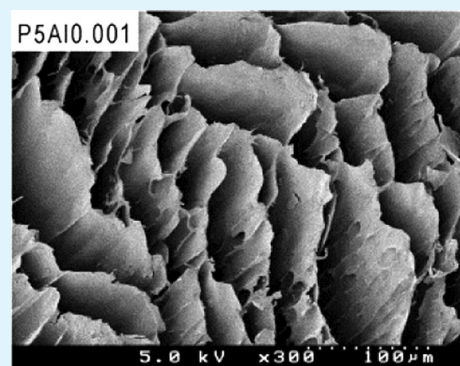
<sup>†</sup>Center for Degradable and Flame-Retardant Polymeric Materials, College of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China

<sup>‡</sup>Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202, United States

<sup>§</sup>Bioproduct Chemistry and Engineering, United States Department of Agriculture, Western Regional Research Center, Agricultural Research Service (USDA/WRRC/ARS), 800 Buchanan Street, Albany, California 94710, United States

**ABSTRACT:** Biodegradable, foamlike materials based on renewable pectin and sodium montmorillonite clay were fabricated through a simple, environmentally friendly freeze-drying process. The addition of multivalent cations ( $\text{Ca}^{2+}$  and  $\text{Al}^{3+}$ ) resulted in apparent cross-linking of the polymer and enhancement of aerogel properties. The compressive properties increased as the solid contents (both pectin and clay) increased; moduli in the range of 0.04–114 MPa were obtained for materials with bulk densities ranging from 0.03 g/cm<sup>3</sup> to 0.19 g/cm<sup>3</sup>, accompanied by microstructural changes from a lamellar structure to a cellular structure. Biodegradability of the aerogels was investigated by detecting CO<sub>2</sub> release for 4 weeks in compost media. The results revealed that pectin aerogels possess higher biodegradation rates than wheat starch, which is often used as a standard for effective biodegradation. The addition of clay and multivalent cations surprisingly increased the biodegradation rates.

**KEYWORDS:** biodegradable, pectin, clay, aerogel



## INTRODUCTION

Biodegradable and biobased polymers are of increasing interest, because of the limits in fossil fuel resources and a variety of environmental problems.<sup>1–3</sup> Such biobased polymers are produced primarily from renewable resources, such as sugar cane, proteins, starches, and plant oils.<sup>4–7</sup> Use of these materials as alternatives to petrochemicals can decrease the overall carbon footprint for consumer and industrial products, as well as reduce their environmental impacts.

Low-density materials, such as petroleum-based polymers foams and balsa wood, find a wide range of commercial uses where product density is an important design criterion. Balsa forests are limited natural resources, and the polymer foams typically require blowing agents and result in nonbiodegradable waste with its attendant environmental problems.

Lignin-based polyols have been reported as feedstocks for polyurethanes.<sup>8</sup> While this polyol is produced from agricultural wastes, the chemical modifications required to convert these materials into feedstocks reduce the overall environmental benefits of such materials. Starch-based foams are well-known and can be used as packing materials, but they possess relatively low mechanical properties.<sup>9</sup>

Pectins are one of the major structural polysaccharide families of higher plant cells. Pectins are white, amorphous, complex carbohydrates that occur in ripe fruits and certain vegetables, and they are available as a byproduct of fruit juice, sunflower oil, and sugar manufacturing. Fruits rich in pectin include peach, apple, plum, and citrus.<sup>10–12</sup> The U.S.

Department of Agriculture (USDA) reports that 1.5 million tons of pectin-rich feedstock is available annually from beets alone; the resultant pectin is of low value at the present time, and the identification of higher value-added applications for this renewable resource should be a focus of current research.<sup>12</sup> This broad availability makes pectins good candidates as feedstocks for environmentally friendly materials. Pectin is well-known for its use in the gelling of solutions (jams and jellies) and for its application in film formation. Gelling is necessary for success in the freeze-drying process desired in the current work, and film formation is at the heart of “house of cards” structure formation. Hence, pectin would appear to be ideal for freeze-drying-based aerogel materials; the use of pectin in coating and wrapping for food and pharmaceutical products further supports this hypothesis. Pectins are anionic polysaccharides based on chains of linear regions of 1,4- $\alpha$ -D-galacturonosyl units and their methyl esters, interrupted in places by 1,2- $\alpha$ -L-rhamnopyranosyl units.<sup>12–14</sup> The carboxyl units along the backbone provide salt responsiveness and allow the formation of hydrogel networks when adding cations.<sup>13</sup> Divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Pb}^{2+}$ ) have been demonstrated to cross-link pectins. Among these ions,  $\text{Ca}^{2+}$  has been studied for its use in the food industry.<sup>15–17</sup> In the present work, utilization of divalent and trivalent cations then raises the

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possibility of supramolecular bonding of chains, and a facile, major modification of mechanical properties by simply adding the desired ions to the aqueous solution used for aerogel production. Such a benign method of cross-linking chains can be expected to be more economical and sustainable than using glycoaldehyde, diisocyanates, and other highly reactive and toxic chemical agents.

We have reported an environmentally benign process for the preparation of polymer/clay materials through a freeze-drying process from aqueous mixtures.<sup>18,19</sup> The successful preparation of a biodegradable foam substitute based on casein and sodium montmorillonite (Na<sup>+</sup>-MMT), with very low density (0.07–0.12 g cm<sup>-3</sup>) and exhibiting good compressive properties (90–5600 kPa) was recently reported.<sup>20,21</sup> Other bio-based aerogels, such as those derived from cellulose and alginate, have also been reported.<sup>22,23</sup>

In the current work, we report another biodegradable, foam-like material, this time based on pectin and Na<sup>+</sup>-MMT. The effects of ionic cross-linking of these materials upon mechanical properties and biodegradation performance are described.

## EXPERIMENTAL SECTION

**Materials.** Pectin (from citrus), sodium chloride, calcium chloride and aluminum sulfate (Fisher Scientific), and sodium montmorillonite (Na<sup>+</sup>-MMT; PGW grade, cation exchange capacity (CEC) 145 mequiv/100 g; Nanocor) were used without further purification. Deionized (DI) water was obtained using a Barnstead RoPure reverse osmosis system.

**Aerogel Preparation.** Percentages of pectin and clay structural components are given as a percentage of solutions to be frozen, in DI water as solvent. Percentages of cationic cross-linkers are relative to the amount of pectin present in the aerogel material.

**Pectin/Clay Aerogel Composites.** To produce a 5% pectin and 5% clay aerogel, for example, 5 g of Na<sup>+</sup>-MMT was blended with 100 mL of DI water on the high-speed setting of a Waring Model MC2 mini laboratory blender for 1 min to obtain a 5 wt% clay aqueous suspension. Five grams (5 g) of pectin powder was then added slowly into the clay gel under constant stirring, to obtain pectin/clay gels comprising 5 wt% pectin and 5 wt% clay (this will be referred to as P5C5, where P stands for pectin, and C stands for clay). The resulting mixture was then poured into polystyrene vials and immediately frozen in a solid carbon dioxide/ethanol bath (approximately –80 °C). The frozen samples were dried in a VirTis Advantange freeze dryer, where a high vacuum was applied to sublime the ice. The freeze-dry process typically was given 3–4 days to ensure complete drying.

**Cationic Cross-Linked Pectin/Clay Aerogel Composites.** An aerogel containing 5% pectin, 5% clay, and cross-linked with calcium (0.001 mol Ca<sup>2+</sup>/g pectin) was produced in the following manner. Eleven grams (11 g) of CaCl<sub>2</sub> was dissolved in 100 mL of DI water to obtain a 1 M solution. As mentioned above, 5 g of pectin, 5 g of clay, and 95 mL of DI water were combined to create pectin/clay gels. Five mL of the calcium chloride solution was then added to a pectin/clay gel with stirring to create homogeneous mixture. The resulting mixtures were then freeze-dried as above. The resulting sample is noted as P5C5Ca0.001.

**Characterization.** The samples were placed in ambient environment (25 °C, humidity: 50%) for 3 days, to make the sample moisture be in equilibrium with the environment before testing.

The densities of the aerogels were calculated from the mass and dimension measurements using an analytical balance and digital calipers.

Compression testing was conducted on the cylindrical specimens (~20 mm in diameter and height), using an Instron Model 5565 universal testing machine, fitted with a 1 kN load cell, at a crosshead of 10 mm min<sup>-1</sup>. Five samples of 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 using a Hitachi Model S-4500 scanning electron microscopy (SEM) microscope at an acceleration voltage of 5 kV. The samples were prepared by fracturing in liquid nitrogen, and then coated with platinum before testing.

The thermal stabilities were measured on a Model TGA Q500 system (TA Instruments) under a nitrogen flow (40 mL min<sup>-1</sup>). Samples (~5 mg) were placed in a platinum pan and heated from ambient temperature to 600 °C at a rate of 10 °C min<sup>-1</sup>.

The biodegradability of pectin aerogels was evaluated by monitoring the CO<sub>2</sub> yield, using a Micro-Oxymax Respirometer System (Columbus Instruments, Inc.). Cylindrical specimens (~0.2 g) were ground and mixed with compost soil and kept in a 250-mL sample chamber at ambient temperature. The degree of biodegradation (*D*, expressed as a percentage) was calculated by the following equation:

$$D (\%) = \frac{V(\text{CO}_2)_t - V(\text{CO}_2)_b}{V(\text{CO}_2)_{\text{th}}} \times 100 \quad (1)$$

where  $V(\text{CO}_2)_t$  and  $V(\text{CO}_2)_b$  represents the amounts of CO<sub>2</sub> released within the assay and the blank reactor, respectively, and  $V(\text{CO}_2)_{\text{th}}$  is the theoretical amount of CO<sub>2</sub> available from the samples.

## RESULTS AND DISCUSSION

**Preparation, Mechanical Property, Density, and Morphology of Pectin/Clay Aerogels.** Freeze drying is a practical method by which to produce polymer aerogel composites. Figure 1 shows aerogel samples based on pectin



Figure 1. Pectin/clay aerogel composite, 2 cm in diameter.

and montmorillonite clay; these materials exhibit stable, workable structures. As the concentration of pectin increase, the pectin solution viscosity increases monotonically, and the color of aerogel turns from light yellow to brown. At high pectin content (e.g., 15 wt%) or when cross-linked with multivalent cations, the aerogels slightly shrink during the freeze-drying process, with a typical diameter of 19.2 mm observed, compared to 20.0 mm for the typical 5 wt% polymer aerogel produced in the same 20.0-mm-diameter polystyrene vial mold. This shrinkage can be attributed to the strong interaction between pectin chains (hydrogen bonds and cross-links).

One set of composite samples produced from a 15 wt% pectin solution (denoted as P15) was prepared to examine the influence of high polymer contents. The high polymer loading of this material made it difficult to dissolve and mix; hence, 15 wt% is the practical limit for pectin solutions used to produce aerogels. Table 1 lists the moduli, density, and specific moduli values for aerogels produced from various levels of pectin and clay. Pure pectin aerogels exhibit very good mechanical properties; for example, with a density of 0.16 g cm<sup>-3</sup>, P15 has a modulus of 48 ± 14 MPa, which is higher than that of

Table 1. Modulus, Density, and Specific Modulus of Aerogels Based on Various Contents of Pectin and Clay<sup>a</sup>

pectin/clay		P2.5	P5	P7.5	P10	P12.5	P15
C0	modulus, <i>M</i>	0.04 ± <0.01	0.07 ± 0.01	0.33 ± 0.08	1.2 ± 0.2	12 ± 5	48 ± 14
	density, <i>D</i>	0.03 ± <0.01	0.06 ± <0.01	0.08 ± <0.01	0.10 ± <0.01	0.13 ± 0.01	0.16 ± <0.01
	specific modulus, <i>M/D</i>	1.3 ± 0.2	1.1 ± 0.1	4.4 ± 1.2	11 ± 2	93 ± 38	302 ± 89
C2.5	modulus, <i>M</i>	0.16 ± 0.03	0.33 ± 0.03	1.2 ± 0.2	6.1 ± 1.3	63 ± 8	101 ± 6
	density, <i>D</i>	0.05 ± <0.01	0.09 ± <0.01	0.10 ± <0.01	0.12 ± <0.01	0.15 ± <0.01	0.16 ± <0.01
	specific modulus, <i>M/D</i>	3.2 ± 0.7	3.9 ± 0.5	12 ± 2	52 ± 11	429 ± 55	617 ± 32
C5	modulus, <i>M</i>	0.29 ± 0.01	1.4 ± 0.3	6.5 ± 0.8	20 ± 5	106 ± 12	114 ± 9
	density, <i>D</i>	0.07 ± <0.01	0.10 ± <0.01	0.12 ± <0.01	0.14 ± <0.01	0.17 ± <0.01	0.19 ± <0.01
	specific modulus, <i>M/D</i>	4.1 ± 0.2	15 ± 3	56 ± 7	145 ± 36	632 ± 66	609 ± 53

<sup>a</sup>P stands for pectin, C stands for clay, and the number after letter represents its weight percentage in the original solution prior to freeze drying.

typical polymer aerogels of similar densities<sup>18–22</sup> and is attributable to strong hydrogen bonding between pectin chains. With increasing aerogel density (i.e., with increasing volume fractions of solid matter within the aerogels as the pectin concentration of the starting solution was increased from 2.5 wt % to 15 wt %), the moduli of pectin aerogels increase significantly, from 0.04 MPa to 48 MPa. That fact that the compressive modulus of such porous/cellular material will increase with increasing density is consistent with prior work in this field.<sup>24</sup> The specific moduli of pectin aerogels (modulus divided by density) increased significantly as the density increased, demonstrating a nonlinear change in structure with increasing polymer content. The morphological microstructures of the pectin aerogels are shown in Figure 2. For composite samples containing 5 wt % pectin (denoted as P5), a layered structure is evident from the SEM images; for

composite samples containing 10 wt % pectin (denoted as P10), the layer thickness increased without obvious structural changes. As the pectin solution concentrations were increased to 15 wt % (P15), the resulting pectin aerogels exhibited a network structure. These structural changes most likely result from the increased solution viscosities. During the freezing process, ice crystals grow while pushing the pectin chains aside into the ice grain boundaries. At low concentrations of polymer, the low viscosity presents little resistance to the growth of an ice front, allowing for the formation of lamellar ice layers. For high-viscosity solutions, growth of the ice layers is retarded by the fluid viscosity, resulting in more fractal growth and secondary crystallization of water and the generation of a greater number of structural links between the aerogel layers.

Clay is used for strengthening such aerogels. Pure clay aerogels can be difficult to handle, having, for example, a compressive modulus of only ~10 kPa exhibited from freeze-dried 5 wt % solutions and layered structures lacking interlayer connections.<sup>20</sup> Polymer/clay aerogels, on the other hand, exhibit good mechanical properties; Table 1 lists mechanical properties for fixed pectin contents, and the compressive modulus is shown to increase monotonously with increasing clay content. For aerogels produced from 5 wt % pectin solutions, the modulus increased from 10 kPa to 330 kPa as 2.5 wt % clay is added. The addition of 5 wt % clay to the 5% pectin solution further increases the aerogel modulus to 1.4 MPa. For the 10 wt % pectin series, moduli of 1.2, 6.1, and 20 MPa are observed as the solution clay content increases from 0 to 2.5 wt % and 5 wt %. However, the incorporation of clay does increase the viscosity of the solutions to be frozen, leading to the formation of network structures. As shown in Figure 2, a layer-network structure change is observed for freeze-dried P10C5, in contrast to the layered structure observed for P5C5. While increasing the clay content in the pectin aerogels does increase the overall bulk densities, the corresponding increases in mechanical properties are greater; hence, the specific moduli (Table 1) of all pectin aerogel series evaluated herein (2.5 to 15 wt % pectin) increase monotonically with increasing clay content. The advanced mechanical properties of pectin/clay aerogels make them promising alternatives in the engineering field.

The compressive moduli of the materials in this study are presented as a function of pectin content in Figure 3a. Typical stress/strain curves are illustrated in Figure 3b. At low solid concentrations, such as P5 and P5C5, the compression curves exhibit classical linear stress–strain, stress plateau, and densification regions. No catastrophic fracture is observed in

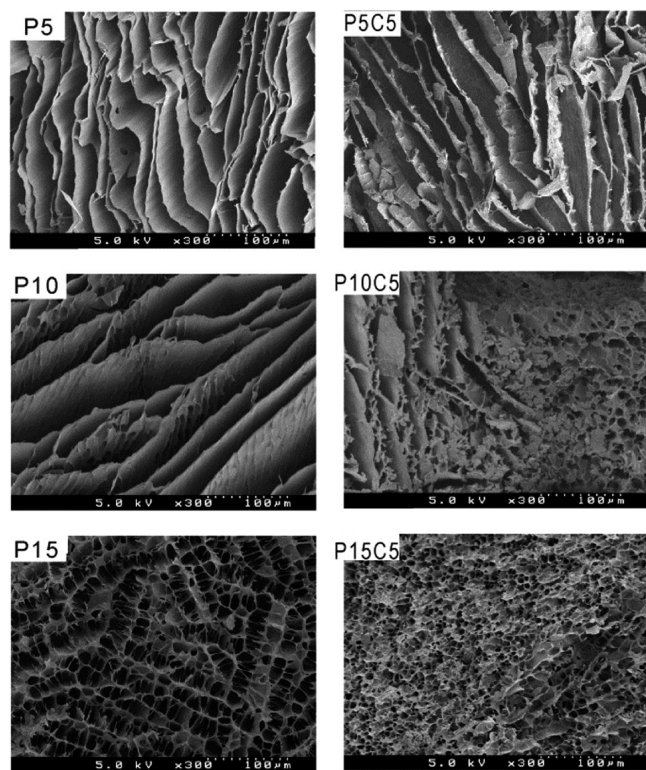
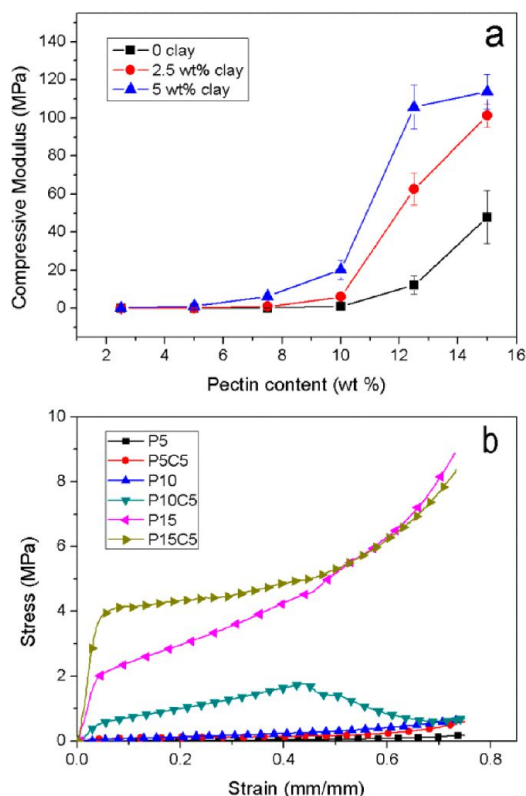


Figure 2. Scanning electron microscopy (SEM) micrographs of pectin and pectin/clay aerogels.

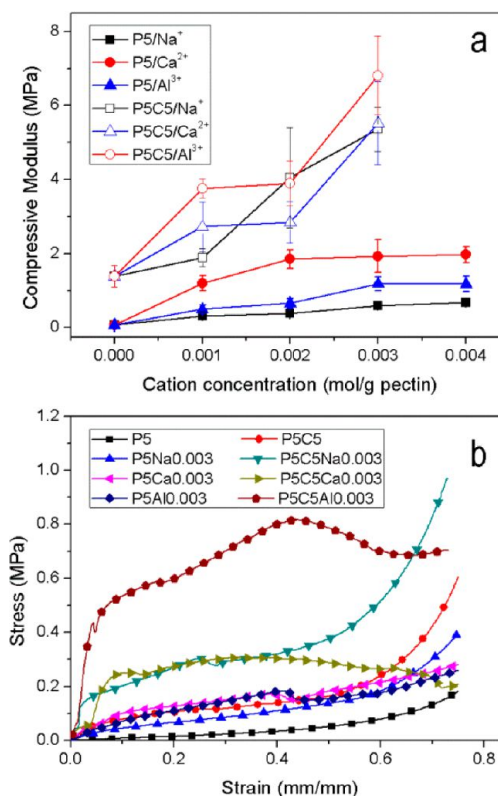




**Figure 3.** (a) Compressive moduli and (b) stress–strain behaviors of pectin/clay aerogels.

these aerogel materials. However, fracture is observed in P10C5. There is no obvious plateau stage during compression for the high-concentration pectin aerogel samples, and their densification stages are observed at lower strain values, because of the high densities of the aerogels.

Pectin has the ability to be cross-linked with cations. This physical cross-linking phenomenon for pectin is widely used in the food industry. Ichibouji et al. used this property for the preparation of membranes, and they found that pectin gels have a tensile strength of 2.4–5.3 MPa.<sup>25</sup> In this study, we chose three cations for cross-linking the pectin aerogels: a monovalent cation (sodium, Na<sup>+</sup>), a divalent cation (calcium, Ca<sup>2+</sup>), and a trivalent cation (aluminum, Al<sup>3+</sup>). The detailed compressive modulus, density, and specific moduli of the cationically cross-linked pectin aerogels are listed in Table 2. The compressive moduli, as a function of pectin content, is illustrated in Figure 4a, and typical stress/strain curves are illustrated in Figure 4b.



**Figure 4.** Compressive moduli (a) and stress–strain behaviors (b) of cationic cross-linked aerogels based on 5 wt % solution content of pectin.

Five weight percent (5 wt %) pectin solutions were chosen for aerogel preparation in an effort to make this effect clearly visible. Four cation concentrations, in the range of 0.001–0.004 mol/g pectin, were chosen to produce optimal cross-linking, based on the prior literature. Sodium showed no ability to cross-link pectin solutions, as one might expect and is consistent with the literature. However, the moduli of pectin increased slightly with increasing sodium salt concentration, presumably due to increasing solid matter and density. Calcium is a widely used cross-linker for pectin in the food industry. With added Ca<sup>2+</sup> ions, the solution viscosity increases significantly. The moduli of Ca<sup>2+</sup>-ion cross-linked aerogels also increased significantly. With the addition of 0.001 mol Ca<sup>2+</sup> per gram pectin, the aerogel modulus increased from 0.07 ± 0.01 MPa for neat pectin aerogels to 1.2 ± 0.2 MPa, then to 1.9 ± 0.3 MPa with 0.002 mol Ca<sup>2+</sup> addition per gram pectin. This

**Table 2. Modulus and Density of Aerogels Based on 5 wt % Pectin Cross-Linked with Various Cations**

		P5/0.001	P5C5/0.001	P5/0.002	P5C5/0.002	P5/0.003	P5C5/0.003	P5/0.004
NaCl	modulus, <i>M</i>	0.32 ± 0.10	1.9 ± 0.2	0.38 ± 0.08	4.1 ± 1.4	0.59 ± 0.07	5.4 ± 0.6	0.68 ± 0.11
	density, <i>D</i>	0.05 ± <0.01	0.10 ± <0.01	0.06 ± 0	0.10 ± <0.01	0.06 ± <0.01	0.10 ± <0.01	0.07 ± <0.01
	specific modulus, <i>M/D</i>	6.0 ± 1.8	20 ± 2	6.6 ± 1.5	41 ± 14	9.4 ± 1.1	53 ± 6	10 ± 2
CaCl <sub>2</sub>	modulus, <i>M</i>	1.2 ± 0.2	2.7 ± 0.7	1.9 ± 0.3	2.9 ± 0.6	1.9 ± 0.4	5.5 ± 1.1	2.0 ± 0.2
	density, <i>D</i>	0.06 ± <0.01	0.10 ± <0.01	0.06 ± <0.01	0.11 ± <0.01	0.08 ± <0.01	0.12 ± <0.01	0.10 ± 0.01
	specific modulus, <i>M/D</i>	21 ± 4	28 ± 7	29 ± 3	27 ± 5	24 ± 6	46 ± 9	20 ± 2
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	modulus, <i>M</i>	0.50 ± 0.12	3.8 ± 0.3	0.66 ± 0.13	3.9 ± 0.6	1.2 ± 0.2	6.8 ± 1.1	1.2 ± 0.2
	density, <i>D</i>	0.06 ± <0.01	0.10 ± <0.01	0.07 ± <0.01	0.10 ± <0.01	0.08 ± <0.01	0.12 ± <0.01	0.08 ± <0.01
	specific modulus, <i>M/D</i>	8.6 ± 2.1	39 ± 3	10 ± 2	37 ± 6	16 ± 3	58 ± 9	15 ± 2

physical cross-linking effect achieves saturation with further  $\text{Ca}^{2+}$ -ion addition. Aluminum is seldom reported for pectin cross-linking, perhaps because of its unacceptable toxicity for food applications. It would be expected that the use of a trivalent cation would exhibit pectin cross-linking well in excess of that observed with calcium. With a loading of  $0.003 \text{ mol Al}^{3+}$  per gram of pectin in the starting solution, the modulus of the finished aerogel increased to  $1.2 \pm 0.2 \text{ MPa}$ , compared to  $0.07 \pm 0.01 \text{ MPa}$  for the un-cross-linked pectin aerogel control. With further additions of  $\text{Al}^{3+}$ , the compressive properties eventually reached saturation, as was the case with use of  $\text{Ca}^{2+}$  ions. Further addition of clay to cationically cross-linked aerogels led to remarkable increases in modulus. This was particularly true for the sodium/clay systems, such as P5C5/Na0.002, wherein the compressive modulus increased to  $4.1 \pm 1.4 \text{ MPa}$ , even higher than P5C5/Ca0.002 ( $2.9 \pm 0.6 \text{ MPa}$ ) and P5C5/Al0.002 ( $3.9 \pm 0.6 \text{ MPa}$ ). These results are not in accordance with the pectin/cation system. It is reported that, at high concentrations, sodium has the effect of exfoliating montmorillonite (MMT) clay, thereby increasing the effective clay concentration.<sup>26</sup> A similar effect has been also observed for the calcium and aluminum cross-linking systems. Among these, the  $\text{Al}^{3+}$  cation exhibited the greatest degree of synergy with clay. The modulus of P5C5/Al0.003 reached  $6.8 \pm 1.1 \text{ MPa}$ , while its specific modulus measured  $58 \pm 9 \text{ MPa g}^{-1} \text{ cm}^3$ . This effect may result from the greater ability of the trivalent cation to exfoliate the clay. Besides the cross-linking, the counterions may improve the interaction between the anionic clay platelets and the anionic polymer, which could also be the possible mechanism of enhanced mechanical properties. Because the existence of cross-links, fracture occurs in stress/strain curves of calcium or aluminum cross-linked aerogel during compression (Figure 4b). The compression strain upon these aerogels is irreversible, and a rigid structure results from cross-linking that lacks enough flexibility.

The morphological microstructures of cationically cross-linked aerogels are illustrated in Figure 5. For cationically cross-linked aerogels, obvious layer structures are observed. Calcium and aluminum cross-linked layers exhibit much rougher surfaces, which may be caused by increased solution viscosities. Layered structure can be distinguished for all cationic cross-linked pectin/clay aerogels. The addition of clay would further increase the solution viscosity and block the ice growth, thus generating a much rougher layer structure (sometimes a network structure can be regarded).

**Thermal Stability.** The thermal stabilities of the pectin, pectin/clay and cation cross-linked aerogels, as shown in Figures 6 and 7, respectively, was investigated by thermogravimetric analysis (TGA). This analysis provided the onset decomposition temperature ( $T_d$ ), percentage of residue ( $W_R$ ), highest weight loss temperature ( $T_{d \text{ max}}$ ), and highest weight loss rates ( $dW/dT$ ) as the samples were heated. Such bio-based materials typically have significant quantities of water associated with them, and they display similar decomposition patterns with two main steps of weight loss. The first weight loss is observed up to  $100 \text{ }^\circ\text{C}$  ( $\sim 10\%$  weight loss), was certainly related to the removal of adsorbed or bond water. The addition of clay or cation would make this stage more obvious, since both clay and cationic compounds easily absorb water. The second weight loss step begins at  $\sim 200 \text{ }^\circ\text{C}$ , which is associated with the decomposition of pectin. Neglecting the first weight loss stage (a measure of bound water, not thermal stability),  $T_d$  (defined as the temperature at which 5% weight beyond loss of

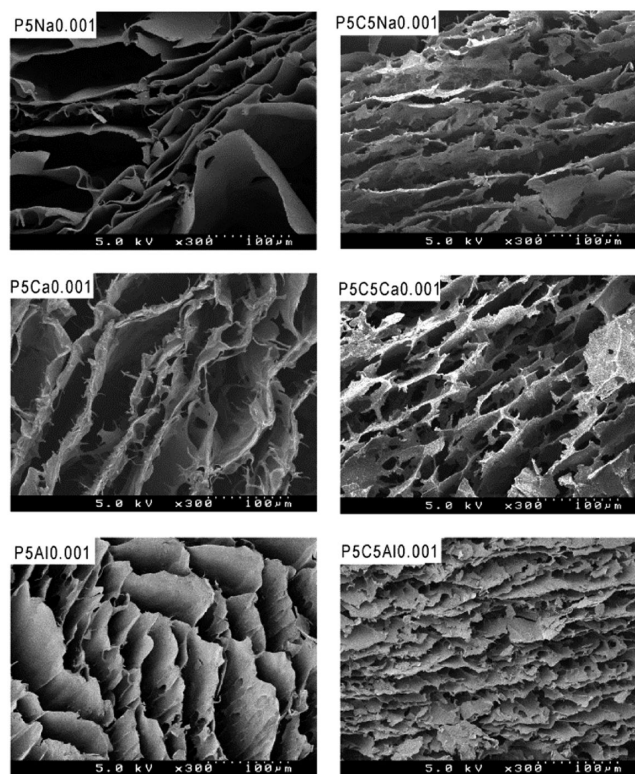


Figure 5. SEM micrographs of 5 wt % pectin aerogels cross-linked with different cations.

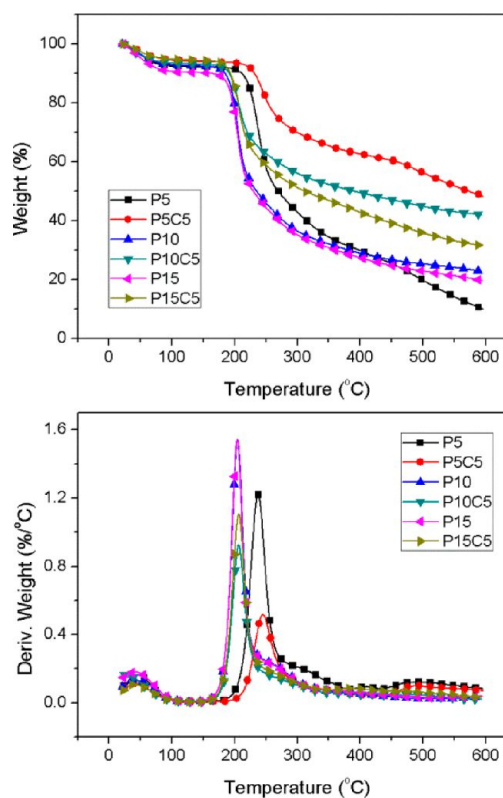
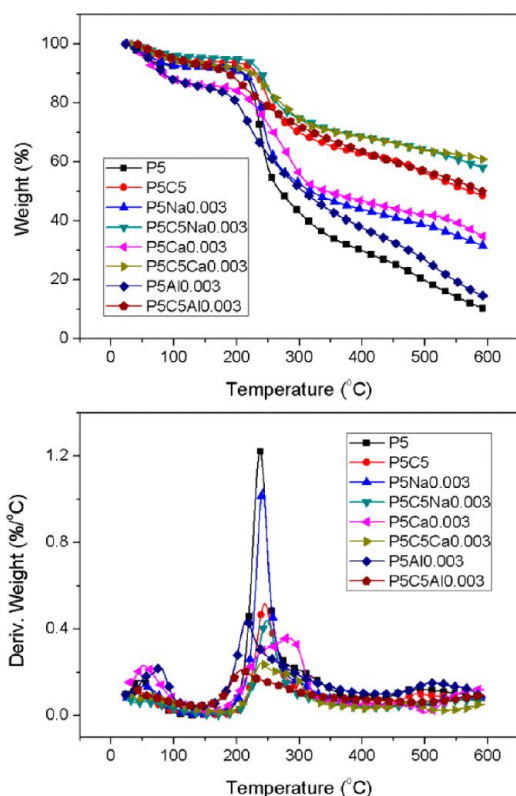


Figure 6. Thermogravimetric analysis (TGA) and differential thermal gravimetry (DTG) curves of pectin/clay aerogels.

water occurred) was recorded to investigate the thermal stability of pectin. The thermal stability of pectin aerogels



**Figure 7.** TGA and DTG curves of pectin/clay aerogels cross-linked with cations.

increased modestly with an increase in clay loading, which was typical for composite materials and was attributed to the thermal insulation effect and mass-transport barriers of clay. Diffusion of decomposition products is hindered by the presence of clay, in part explaining the TGA results. There appeared to be insufficient pectin for P5 to produce complete interpenetrating co-continuous networks; therefore, this system exhibited inferior thermal stability, compared to that of high-density pectin aerogel.

The thermal stability of cationically cross-linked aerogels increased slightly (compare the sodium and calcium series in Table 3), which is consistent with vitrification of these systems. Decreased thermal stability of aluminum-cross-linked pectin was observed and is likely caused by the bonding water in the

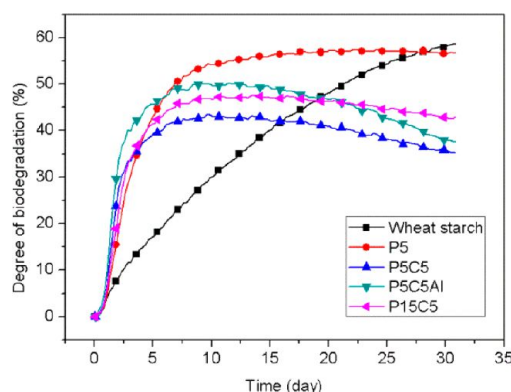
**Table 3. Thermal Characteristics of the Freeze-Dried Aerogels**

sample	$T_d$ (5% from 150 °C)	$T_{d\max}$ (°C)	$dW/dT$ (%/°C)	residue (%)
P5	220.6	237.7	1.22	10.0
P5C5	234.9	244.6	0.52	48.3
P10	191.1	205.0	1.54	22.7
P10C5	194.5	206.7	0.93	42.0
P15	191.3	204.2	1.53	19.7
P15C5	194.7	206.9	1.11	31.4
P5Na0.003	224.4	241.8	1.05	31.3
P5C5Na0.003	238.2	248.5	0.44	57.7
P5Ca0.003	221.1	277.8	0.36	34.3
P5C5Ca0.003	235.4	239.3	0.24	60.7
P5Al0.003	199.7	216.0	0.44	14.3
P5C5Al0.003	200.0	208.3	0.21	49.6

aluminum sulfate additive; this leads to a continuous weight loss during heating from 86.5 °C to 250 °C.

The trends observed for  $T_{d\max}$  followed those of  $T_d$ , although the highest weight loss rate observed was different. P10 and P15 gave the highest peak weight loss rates; these values decrease with the addition of clay or metal cations. The rate of degradation for P5 decreased from 1.22%/°C to 0.36%/°C with the addition of Ca(0.003), indicating that physical cross-linking retards thermal degradation of the pectin aerogels. The formation of a carbonaceous surface layer during TGA analyses could protect the material under surface, leading to incomplete decomposition of pectin aerogels with residual yields of 10.0%–60.7%. The residue of aerogel also increased with the addition of clay and cations.

**Biodegradation.** The biodegradation property of pectin aerogels and pectin/clay aerogel composites were obtained in compost media at room temperature. The corresponding curves are illustrated in Figure 8. Wheat starch was chosen as a



**Figure 8.** Degree of biodegradation of the pectin and pectin/clay aerogels in compost media.

reference for its good biodegradability (~60% after 30 days). Pectin aerogels and pectin/clay aerogel composites exhibited even better biodegradability than wheat starch. Their degrees of biodegradation reached 40%–57% after 10 days of immersion in compost media, while, at the same time, wheat starch reached only 30%.

Most of the aerogels exhibited similar biodegradation behaviors. During the first 5 days, the samples degraded very fast and a subsequent plateau occurred after ~10 days. However, the biodegradation rate of P5C5, P5C5Al, and P15C5 was higher during the first few days, compared with that of neat pectin aerogel samples (P5). This indicates that the addition of clay and  $Al^{3+}$  resulted in a higher biodegradation rate. TGA results show that clay and cations would make the sample more hydrophilic. Water is necessary for the living of microorganisms and samples with high moisture help the propagation of microorganisms, which increases the biodegradation rate. Furthermore, the existence of clay and salt in aerogel may change the integrity of the pectin aerogel, causing more defects, thus promoting the biodegradation process.

## CONCLUSIONS

The fabrication of low-density aerogels with bio-based, renewable pectin and clay was demonstrated using environmentally friendly water as the solvent and freeze drying as the production process. Different cations were shown to cross-link pectin during aerogel preparation; the cross-linking ability of



cations is  $\text{Ca}^{2+} > \text{Al}^{3+} > \text{Na}^+$ , with no obvious morphology change observed by SEM with these samples. A synergistic effect was observed when adding clay. With 5 wt % pectin, 5 wt % clay, and 0.003 mol cation/g-pectin, the modulus of aerogel with  $\text{Al}^{3+}$  exhibited the highest modulus of  $6.8 \pm 1.1$  MPa. These materials exhibit overall mechanical properties similar to those of rigid polyurethane foams and balsa-like products, which makes them promising for engineering applications. The compressive moduli of these aerogels increase as the solid contents (both pectin and clay) increase, which is accompanied by a change in microstructure from a layered morphology to network morphology. Aerogels containing 15 wt % pectin and 5 wt % clay exhibit a modulus of  $114 \pm 9$  MPa and a specific modulus of  $609 \pm 53$  MPa  $\text{cm}^3 \text{g}^{-1}$ . Thermogravimetric analysis (TGA) revealed that these aerogels present two weight-loss steps: one associated with a loss of absorbed water, and one associated with a breakdown of the polymer. Biodegradation study in compost media demonstrated higher biodegradation rates of pectin aerogels than that of wheat starch. The addition of clay and salt further increased the biodegradation rates.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: das44@case.edu.

### Notes

The authors declare the following competing financial interest(s): D.S. and CWRU own equity in a startup company that potentially could commercialize this technology. This is noted in the manuscript as well.

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