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Foam-Like Polymer/Clay Aerogels Which Incorporate Air Bubbles

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ABSTRACT: The structure/property relationships of polymer/clay aerogels interfused with uniformly distributed air bubbles were examined. Through the incorporation of a polyelectrolyte in a montmorillonite(MMT) clay solution, the viscosity was systematically changed by the addition of ions with different charges. The bubbles were achieved via high speed mixing and were stabilized through the use of the surfactant sodium dodecyl sulfate (SDS). As the charge of the ion increased from +1 (Na^+ ions) to +2 (Ca^{2+} ions) to finally +3 (Al^{3+} ions), the modulus of the resultant aerogels increased. The foamed polymer/clay aerogels showed a reduction in thermal conductivity while retaining similar mechanical properties to unfoamed polymer/clay aerogels. The most promising composition was one which contained 5% MMT clay/5% poly(vinyl alcohol)/0.5% xanthum gum/0.5% SDS/0.2% $Al_2(SO_4)_3{\cdot}6(H_2O)$ possessing a density of 0.083 g/cm^3, an average modulus of 3.0 MPa, and a thermal conductivity of 41 W/m·K. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39546.

KEYWORDS: foams; mechanical properties; thermal properties

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INTRODUCTION

Polymer/clay composites have been an area of extensive research that has resulted in several commercial products. These composite materials typically rely upon exfoliation of layered, smectite clays, such that individual clay platelets are dispersed within a polymeric phase, generating a network which can transfer physical loads, and can serve to create both polymer crystallization and confinement.[1] The requirement of exfoliation (typically an endothermic step) and the generally high level of incompatibility of silicates with organic polymers, make producing useful composites in this manner difficult.

Aerogels typically are porous inorganic materials composed primarily of air, with skeletal framework structures. Silica is the material most commonly converted to aerogels. Silica aerogels have been utilized in applications ranging from sensors, catalyst supports, thermal/acoustic insulation, and as collection media for particles found in space.[2,3] Applications dictating the use of an extremely low-density material were the catalyst for the use of aerogels in the aforementioned applications. Unfortunately, these materials suffer from high manufacturing costs. The structural features of highly compressible "gel skeletons" produced by vacuum sublimation of frozen thixotropic clay gels in water or benzene were first described by Weiss,[4] Hofmann,[5] and Norrish.[6] Processing parameters for clay aerogels, and the definition of a structure in which clay particles are linked edge-to-face much like a "house of cards" owing to opposite surface and edge charges that exist in clays were reported by van Olphen.[7] The effects of process parameters, such as clay concentration and freezing rates, upon the size and shape of resultant clay aerogels were investigated by Nakazawa.[8] Building on this, a reproducible method of producing organically modified clay aerogels has been followed for this research.[9]

Typical drawbacks of clay aerogels in comparison to silica aerogels are the lower mechanical properties, particularly in compressive testing as well as higher thermal conductivities.[10] The method commonly used to improve the properties of the clay aerogels is incorporating a polymer into the clay aerogel, resulting in a composite with similar densities and structures, but improved mechanical properties.[11–15] One could postulate that the thermal conductivities of polymer/clay aerogels could be reduced to levels approaching those of silica aerogels through the incorporation of uniformly distributed bubbles of air of nearly unvarying diameters into the aerogel precursor. After freeze-drying, the entrapped bubbles would then end up creating controlled voids in the aerogel structure. Added dimensions of difficulty arise from the dynamic duality of the simultaneous expansion of water and contraction of air during the freezing process. Concurrent to this obstacle is the secondary goal of maintaining the existing level of mechanical properties produced in standard polymer/clay aerogels.

Bubbles at equilibrium join together to form structures in which sets of threes individual bubbles come together in trigonal geometries at equal 120° angles.[16] Traditional bubble theory dictates that bubbles form when jostling liquid molecules create

Table I. Compositions of Foamed Aerogel Samples

Sample	MMT (g)	Poly(vinyl alcohol) (g)	Xanthum gum (g)	SDS (g)	Salt	Water (g)	Density (g/cm^3)
A	2.50	2.50	–	–	–	50.0	0.545
B	2.50	2.50	0.25	0.25	0.1 g NaCl	50.0	0.668
C	2.50	2.50	0.25	0.25	0.1 g $Ca(C_2H_3O_2)_2{\cdot}6H_2O$	50.0	0.763
D	2.50	2.50	0.25	0.25	0.1 g $Al_2(SO_4)_3{\cdot}6H_2O$	50.0	0.827

pockets of low density in the liquid containing fewer molecules than surrounding regions. Most of the time, other molecules will just rush in to fill in these air pockets. However, an exodus of molecules can also occur, causing the pockets, or bubbles, to grow.[17] Owing to hydrodynamic break-up, the upper limit of bubble diameter in aqueous systems is approximately 1 cm.[16] The larger the bubble, the less approximate the spherical shape will be owing to hydrodynamic distortions. Bubbles of up to roughly 1 mm in diameter are essentially spherical. Therefore, it is important that the bubbles created within the aerogels are less than 1 mm in diameter. This study explores the potential for incorporating air bubbles into polymer/clay aerogels, and the effects of these bubbles on mechanical and thermal properties of these low-density materials.

EXPERIMENTAL

Materials

Sodium montmorillonite (MMT; Southern Clay, Cloisite® Na$^+$) was used as the clay mineral in preparation of all aerogels. Poly(vinyl alcohol) $M_w = 195{,}000$ g/mol (Sigma-Aldrich) was the polymer used to reinforce the matrix of clay platelets. Sodium chloride and sodium dodecyl sulfate (SDS) (Fisher Scientific), calcium acetate hexahydrate and aluminum sulfate hexahydrate (Sigma-Aldrich), and xanthum gum (Vanderbilt Minerals) were all used as received. SDS was used as a surfactant to compatibilize the bubbles and stabilize their volume. SDS was vital to maintaining nearly consistent bubble diameters uniformly distributed throughout the polymer/clay matrix.

Aerogel Preparation

Clay aerogels were prepared as published previously.[9] Polymer/clay/water gels containing 1–10 wt % solids were produced in a Waring Laboratory model blender (free range speed, 22,000 rpm) for 3–5 min. The resulting gel suspensions appeared homogeneous, with no evidence of phase separation over the duration of their use. The gel suspensions were poured into 18 dram polystyrene vials and submersed in a solid carbon dioxide/ethanol bath at −70°C. Once frozen, the samples were placed into a SP Scientific Virtis AdVantage 2.0 Bench Top Lyophilizer, serial number 218844. The shelf temperature was set to −70°C, the condenser coil was set to −85°C. Once a vacuum of 40 μbar was achieved, the temperature of the shelf was set to 25°C to sublime the water from the frozen gel suspensions. After 72 h, all samples were removed from the freeze drier, and the resultant polymer/clay aerogels were characterized. Two 12″ × 12″ × 1″ panels were prepared in a Millrock Technologies RD-85 commercial freeze drier equipped with four shelves (8 sq ft of shelf space) and a 30-L condenser; the aerogel precursor was poured into thin-walled aluminum molds which were then frozen on a cold-plate cooled with solid carbon dioxide and methanol.

Mechanical Testing

Once freeze dried, the resultant cylindrical aerogels (approximately 20 mm in diameter and 45 mm in height) were tested using a MTS (model 2525 ReNew upgrade package 5565) tensile instrument equipped with a 1000 N load cell. As standard with mechanical testing carried out on aerogels, their properties under compression were tested. To prepare the aerogels for compression testing, each was cut to a height of 20 mm using a band saw. A total of 10 samples for each formulation were tested, with the exception of the control which had two samples tested. The ultimate strain was set to a value of 0.85, that is 85% of the total linear distance.

Rheological Testing

Viscosity testing was performed using a ThermoScientific Haake Mars II Rheometer. The viscosity was tested in rotational mode using a titanium cone with a 2° draft and flat plate. It was important to determine the viscosity as it provided additional data concerning the effects of multivalent ion addition on the gels before they were frozen; as soon as the gels were prepared, their viscosities were determined. Approximately, 5 mL of the gel was required for testing. The frequency of the rotation speed was set to sweep from 0.1 to 100 s^{-1}.

Thermal Conductivity *Testing*

Thermal conductivity was measured using a LaserComp Fox 314 heat flow meter. The testing was performed at a mean temperature of 22.5°C. The Fox 314 machine conforms to ASTM C518-Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus.

RESULTS AND DISCUSSION

A series of poly(vinyl alcohol)/clay aerogel materials, modified by the addition of xanthan gum and metal ions, were prepared (Table I) and tested to determine the effect of the increase in ionic strength on the resulting viscosities and mechanical properties. Xanthum gum was used as a rheological control during bubble formation. This additive is typically used as a rheological control agent for aqueous systems, most often to increase the viscosity in food preparation, or to stabilize emulsions. Xanthum gum forms a colloidal network of intermolecular hydrogen bonding among the helical rod segments.[18] This hydrogen

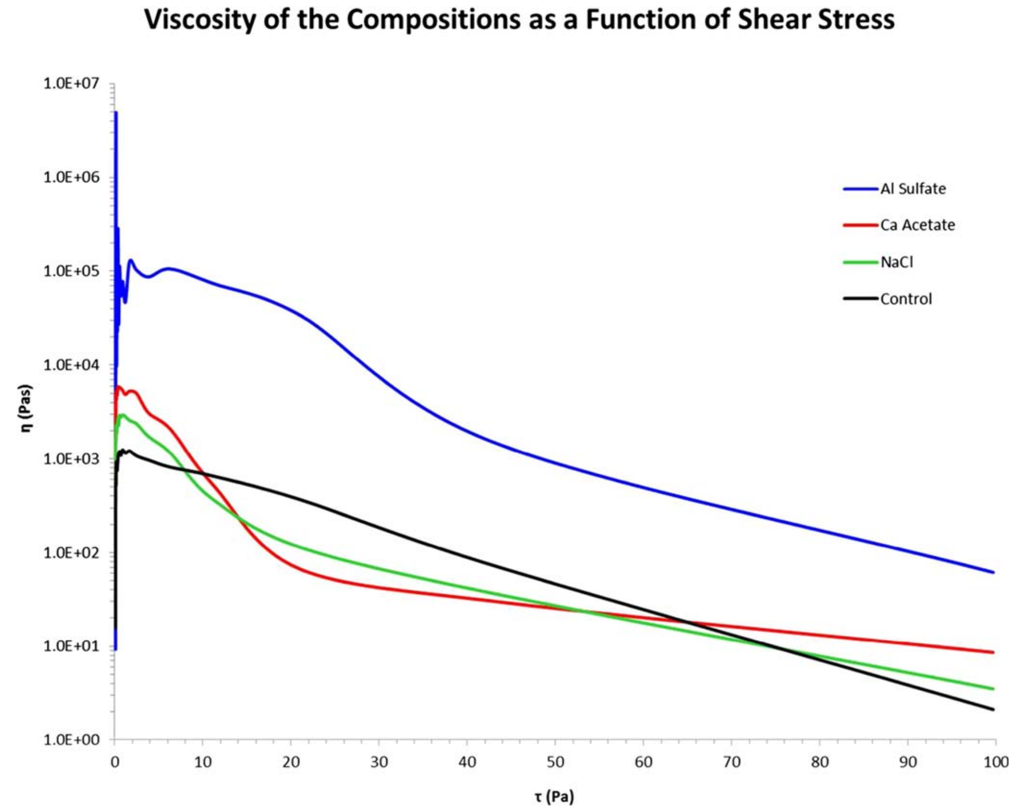

Figure 1. The viscosities of the compositions as a function of shear. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bonding, coupled with limited chain entanglement, produces a highly viscous system.

Xanthum gum is a polyelectrolyte carbohydrate, and therefore an increase in the ionic strength of the aqueous solution will result in an increase in viscosity. Various salts were used to increase the ionic strength and viscosity, with the intent of better stabilizing air bubbles to be entrapped in the gel during suspension production and subsequent freezing.

Solution viscosities increased as the charge of the metal ions was increased; it is to be expected that an increase in the ionic strength of a polyelectrolyte solution will increase the viscosity and mechanical strength of the solution through strong ionic interactions between the pendant groups of the main chain. Thus, as the ionic charge increases from a monovalent ion, Na^+ to a divalent, Ca^{2+} to ultimately a trivalent ion, Al^{3+} the viscosity and mechanical strength should increase monotonically. The aluminum sulfate formulation continued to have the viscosity of a paste several hours and days after creation. As shown in Figure 1, the solution modified by Al^{3+} had a significantly higher viscosity.

A significant observation can be made from the features of the curves. Looking only at the control (Sample **A**), the curve shows a typical non-Newtonian shear-thinning fluid. As the shear stress increases, there is a steady, nearly linear downward trend. All of the other curves display a similar non-Newtonian shear-thinning fluid as well; however, they also display an interesting feature observed in highly foamed systems, where a dramatic change in the slope is observed. This is attributed to the collapse of the foam matrix as the air bubbles merge together and are expelled from the matrix. Once the bubble cellular structure has collapsed, the curves once again display a typical non-Newtonian shear-thinning fluid.

Bubble Formation

It was observed that, owing to an increase in viscosity, a stabilized open-cell foam structure could be produced. This novel aerogel structure may lead to the production of polymer/clay aerogels with a reduced thermal conductivity. Therefore, it became important to create and characterize foamed aerogels through mechanical and SEM imaging. As shown in Figure 2, a foam-like structure with uniform bubble diameters was created and is quite consistent with an average diameter of approximately 100 μm. Equally important is the consistent distribution of the bubbles within the overall structure. This foamed polymer/clay aerogel can be created, with the proper formulation, simply by mechanical shearing at a high shear rate (∼12,000 rpm).

The second issue addressed, after bubble formation, was achieving a uniformly distributed bubble system. It was important to ensure that the bubbles would not agglomerate and form large defects in the aerogel matrix. This issue was solved through the use of a surfactant. The surfactant acted as a compatibilizing agent allowing the bubbles in the gel matrix to form a uniform

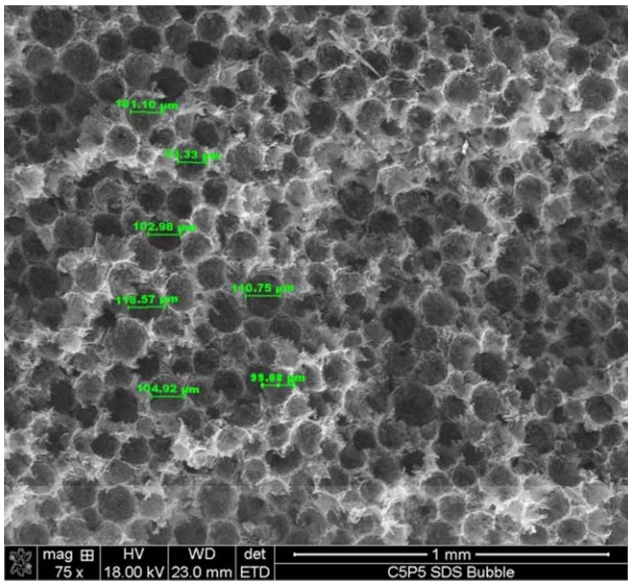

Figure 2. SEM image at magnification of 75×, showing the internal foam structure of Composition D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersion. SDS was chosen because it is a readily available, inexpensive surfactant. Once again, based on the SEM image shown in Figure 2, the SDS proved to be an effective compatibilizing agent.

Typically, it is difficult to overcome the expansion/contraction duality of the foamed mixture during the freezing process in a typical polymer/clay aerogel solution. It is universally known that water expands during freezing and air contracts. It was therefore determined that the viscosity of the mixture and the strength of the walls between the bubbles must be increased to prevent the migration of the bubbles during freezing and maintain the uniformity of the cellular structure. The viscosity modifier, xanthum gum, with added salts was effective at augmenting the viscosity to support the desired cellular foam structure.

This type of open-cell structure was compared with a standard 5% MMT clay/5% PVOH aerogel. To ensure that a bubbled solution did not form in the control sample, first a 10% by weight solution of M_w of 195,000 PVOH and water was created. Next, 25 mL of deionized water and 2.50 g of MMT clay were measured and mixed in a Waring Laboratory model blender (free range speed, 22,000 rpm) on high for 3 min. The 10% MMT clay solution was added to 25 mL of 10% PVOH solution, thusly creating a 5% MMT clay/5% PVOH solution. Once combined, the solution was mixed with a low-speed hand mixer until homogenous.

Mechanical Testing

The freeze-dried, open-cell foam-like compositions were compression tested to compare their respective moduli and toughness. In comparison to the control sample, a standard MMT clay/PVOH aerogel (Table I, Sample **A**), all compositions had a higher modulus and greater toughness. Unfortunately, this did come at the cost of a higher density. It is interesting to note that although the aluminum sulfate-containing sample did have the highest modulus, as predicted, it did not exhibit the greatest toughness. The sample containing NaCl showed the greatest toughness among the compositions as shown in Figure 3. Figure 4 clearly mirrors the trend observed from the viscosity data. As the charge increases, the modulus increases as well. Figure 5 shows the specific moduli of the samples prepared, dividing the moduli by the sample densities to account for densification of materials (it is well established that denser polymer/clay aerogels

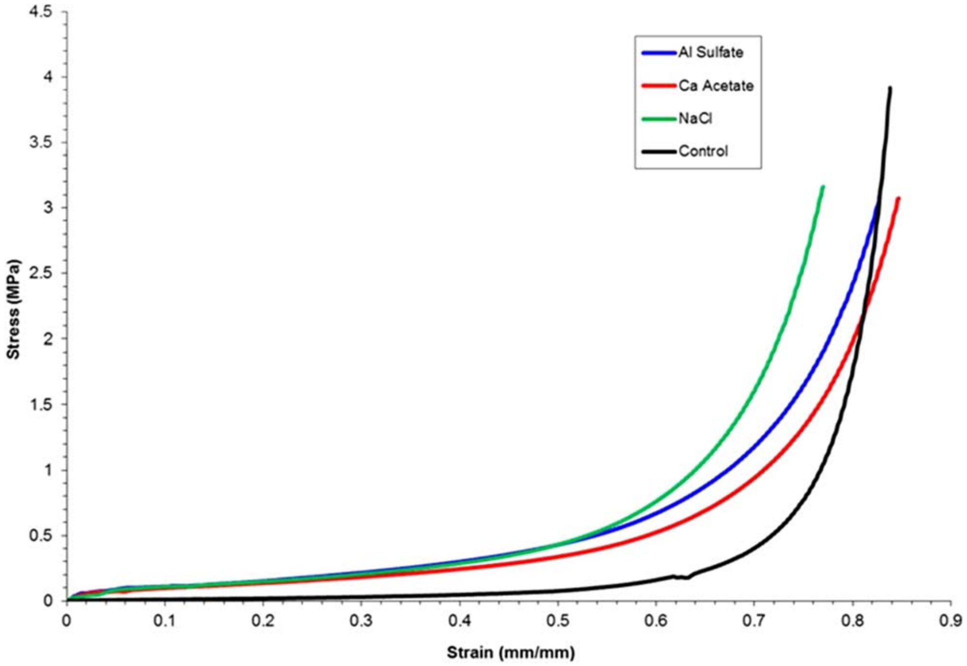

Figure 3. Compressive stress versus strain curves for the aerogel compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

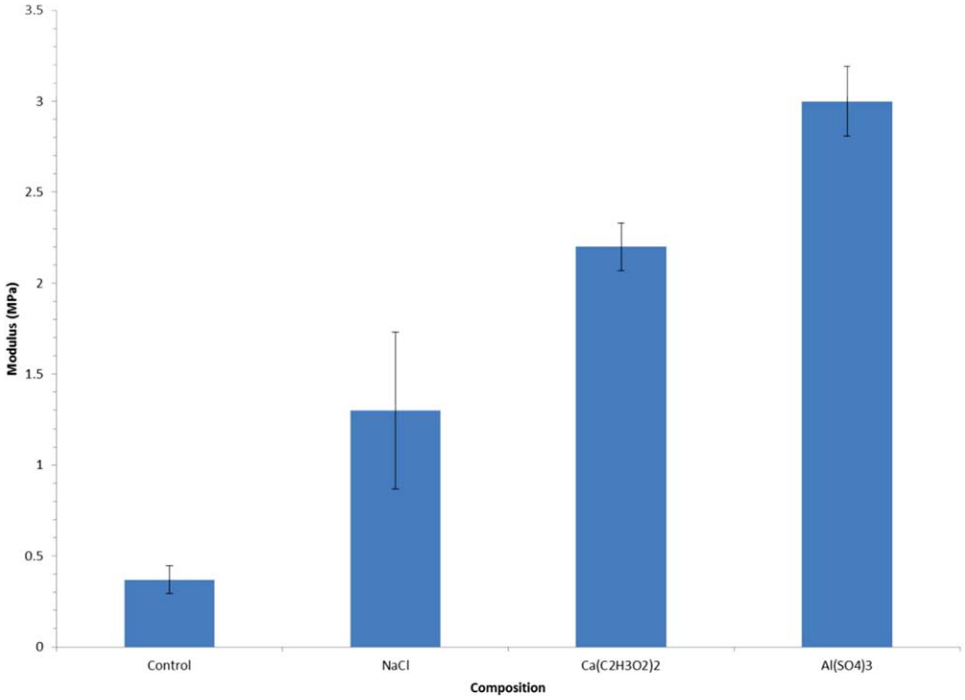

Figure 4. Comparison of the moduli (MPa) of the compositions. The number of samples (n) tested were $n = 2$ for the control, $n = 10$ for the sodium chloride, calcium acetate, and aluminum sulfate compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

generally exhibit greater mechanical properties). As with the moduli, the specific moduli directly reflect the sample viscosities and the progression from mono- to di- to trivalent salt addition.

Thermal Conductivity Properties

The control MMT clay/PVOH aerogel containing 5% clay/5% PVOH (Sample **A**) exhibited a thermal conductivity of 52 W/m·K, whereas Composition **D** showed an average thermal

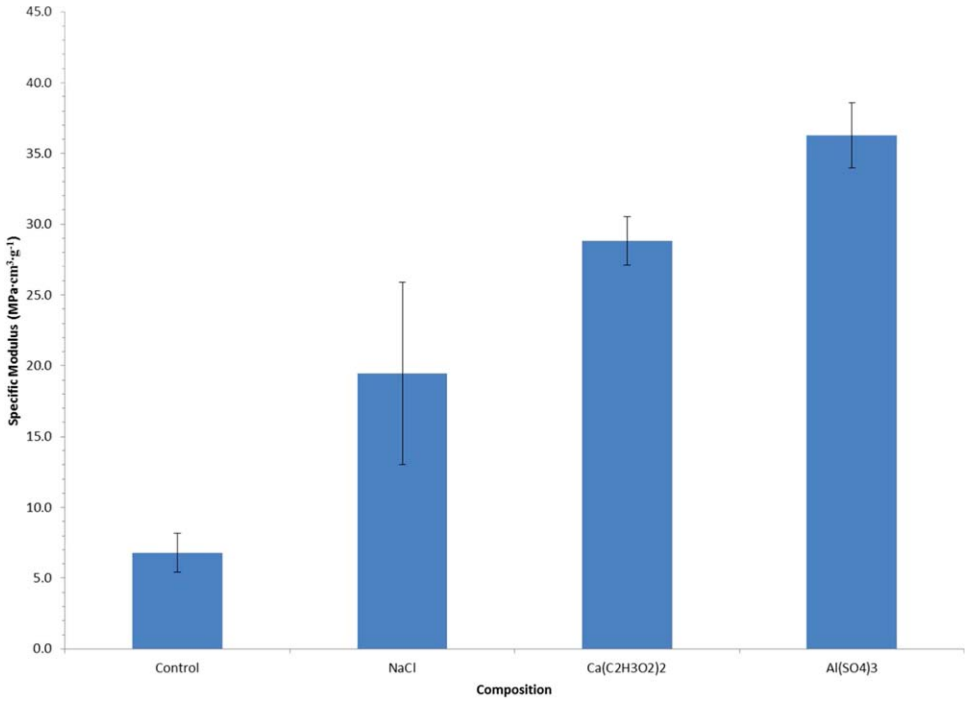

Figure 5. Comparison of the specific moduli (MPa $cm^3 \cdot g^{-1}$) of the compositions. The number of samples (n) tested were $n = 2$ for the control, $n = 10$ for the sodium chloride, calcium acetate, and aluminum sulfate compositions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conductivity of 41 W/m·K, a reduction of 22%. Hence, although the density of the aerogel increased from 0.055 to 0.083 g/cm^3 in the aerogel samples, the bulk thermal conductivity decreased. This counter-intuitive trend in density versus thermal conductivity can be attributed to the incorporation of air bubbles into the composite matrix, lowering the average thermal conductivity of the material.

CONCLUSIONS

Foam-like polymer/clay aerogels can be created and stabilized through the use of viscosity modifying agents such as xanthum gum which increases the viscosity to the point that bubbles will remain trapped within the polymer/clay matrix during the freeze-drying process used to produce aerogels in this study. This study was carried out with the express intent to reduce the thermal conductivity. The most promising composition was one which contained 5% MMT clay/5% poly(vinyl alcohol)/0.5% xanthum gum/0.5% SDS/0.2% $Al_2(SO_4)_3 \cdot 6(H_2O)$ possessing a density of 0.083 g/cm^3, an average modulus of 3.0 MPa, and a thermal conductivity of 41 W/m·K. Incorporation of salts into the polymer/clay solutions prior to freeze drying increased the ionic strength of the polyelectrolyte, both increasing the viscosity, as well as increasing the mechanical properties of the aerogels by as much as a factor of 8; mechanical property enhancements do, however, come at the cost of increasing sample density.

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