Mineralization of Clay/Polymer Aerogels: A Bioinspired Approach to Composite Reinforcement

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ABSTRACT Clay aerogels, ultra low density materials made via a simple freeze-drying technique, have shown much promise in broad applications because of their low densities, often in the same range as silica aerogels (0.03−0.3 g/cm^3,) but suffering from low mechanical strength. A bioinspired approach to mineralize an active polymer/clay aerogel composite is inspected, showing marked improvement of the mechanical properties with increasing modification. Further property improvement was achieved using a layer-by-layer approach to produce alternate layers of polymer and silica on the surface.

KEYWORDS: Mineralization • Composite • Aerogel • Poly(ethylene imine): Clay: Reinforcement

INTRODUCTION

Layered silicates have been used extensively over the past 20 years as an affordable and renewable source of reinforcement in nanocomposites, clays such as sodium montmorillonite being at the forefront of these efforts (1−3). Recently, it has been found that the layered silicates, through a simple and environmentally friendly process, can be converted into aerogels with ultra low densities (0.05−0.1 g/cm^3) (4−10). Their unique house of cards structure, generated by a rearrangement of the clay during freeze-drying, offers many different benefits ranging from thermal insulation properties to an extremely large surface area for efficient catalysis reactions. Although these materials can be very beneficial, most suffer from a lack of mechanical strength without reinforcement.

Incorporation of organic materials into the inorganic framework of clay aerogel materials has been used as a means of enhancing mechanical properties. A variety of water-soluble polymers can be incorporated into the original solutions before freezing so that the polymers are included in the rearranged house of cards structure (5−7, 9). Many porous composites, clay aerogels included, have also benefitted from reinforcement from natural and synthetic fibers (8). Another method of reinforcement has been the cross-linking of organic precursors within the template of the material, imparting low hysteresis loss behavior in the reinforced composite material subjected to repeated stress application (5, 7). All these efforts have yielded success to a degree, and all retained the low density that gives this material its most valuable attribute.

Biomineralization is a natural process of building intricate inorganic−organic composites for improved structural integrity, sensory perception and other biological functions (11, 12). Mineralized systems generally consist of complex hierarchical structures with alternating layers of minerals surrounded by a polymer. Silica mineralization in diatoms employ lysine based proteins to selectively uptake silicic acid from seawater and condense this to an amorphous silica exoskeleton (13−19). Many polyamines have been investigated to determine their silica forming ability including polylysine, poly(allyl amine) and poly(ethylene imine) (17−21). Similar approaches have been used to increase the chemical and mechanical stability of polyesters as well (22). Of these systems, poly(ethylene imine) (PEI) has shown the ability to direct silica formation from pure alkoxysilanes with the help of a catalytic amount of water almost instantaneously, requiring little time in solutions for systems sensitive to water (23, 24). PEI has also been shown to have strong interactions with 2:1 layered silicates such as sodium montmorillonite (25−28).

The present work describes the production of PEI/Clay aerogel and the subsequent mineralization of this composite by condensation of tetramethyl orthosilicate (TMOS) with the polymer backbone, and the resultant enhancement of the mechanical properties of the aerogels. The effects of layering PEI and silica were also investigated.

EXPERIMENTAL SECTION

Materials. Tetramethyl orthosilicate (>98%, TMOS), lithium chloride (>99%), acetone (≥99.5%), and methanol (≥99.8%) were purchased from Sigma Aldrich Co. and used as received. Branched poly(ethylene imine) (B-PEI) with M_w = 1800 and linear poly(ethylene imine) (L-PEI) with M_w = 2500 were purchased from Polysciences, Inc. and used as received. Sodium montmorillonite (PGW) was obtained from Nanocor Inc. and used as received. Deionized (DI) water was obtained using a Barnstead Nanopure low pressure, reverse osmosis purification system.

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Preparation of Aerogels, Silicification, and Subsequent Layering. Five grams of sodium montmorillonite (PGW) was slowly added to 45 g DI water while mixing by hand to wet clay, then the mixture was transferred to a Waring model MC2 mini laboratory blender and mixed at high speed for approximately 1 min. Five grams of B-PEI was added to 50 mL of DI water to produce a readily soluble mixture. The B-PEI solution was slowly added to the clay gel for a final 1:1 ratio of 2.5 wt % clay:B-PEI. The resulting hydrogels were then transferred to 2 cm diameter cylindrical vials and immediately frozen in an ethanol-dry ice mixture. Frozen samples were transferred to a VirTis AdVantage@ EL-85 freeze-dryer and subjected to very high vacuum to sublime the ice for 5 days. Resulting aerogels were cut into similar dimensions using a band saw and placed in desiccator until silicification.

Samples were taken out of desiccator and placed in a $\sim$80% relative humidity (RH) chamber prepared by dissolving 17.73 g of LiCl in 100.00 g of H_2O, sealed, and left for 3 days to equilibrate. Aerogels were removed from the humidity chamber and placed in small vials which were then filled with neat TMOS and allowed to react for 30 s. After reaction, further reaction was limited by immediate and thorough rinsing with acetone. Samples were then allowed to dry in air overnight and placed back in the desiccator for further drying until characterization or subsequent layer.

For layering of the silicified aerogels, 2 g of linear PEI (L-PEI) was dissolved in 200 mL of methanol to produce a 1% solution. Samples were taken out of the desiccator and immediately placed in small vial with 10 mL of the 1% PEI solution and allowed to soak for 20 min. Samples were taken out of the solution and placed in a vacuum chamber heated at 60 °C to drive the solvent off and leave the adsorbed L-PEI. Samples were then placed in the humidity chamber for 3 days and subsequently silicified in the same conditions with TMOS. Subsequent layers were deposited in the same method.

Characterization of Materials. Compression testing was conducted using an Instron 5500 Universal Testing Machine equipped with a 1kN load cell. All compression testing was performed at a constant strain rate of 1 mm/min, with three replicate tests for each set of samples. Imaging was performed on Pd-coated samples using Philips XL-30 Environmental scanning electron microscope.

RESULTS AND DISCUSSION

In the investigation of mineralization as a method of a reinforcement of clay aerogels it is useful to have the mechanical properties of virgin aerogels along with some standards in reinforcement. Previous studies have shown clay aerogels produced from a 5 wt % solution in water without reinforcement to have an initial modulus of 10 kPa and have a density close to 0.05 g/cm (3−9). Reinforcement of a clay aerogel by addition of a polymer to the architecture should ideally incorporate a clay-interactive polymer, but also should be water-soluble to be processed into an aerogel in the same manner. Poly(vinyl alcohol) with a M_w = 85 000−124 000 has been shown to exhibit strong interactions with montmorillonite (6), and was quite advantageous when added to the initial mixture, raising the initial modulus more than one hundredfold to 1.6 MPa.

Poly(ethylene imine) has been demonstrated to strongly adsorb to clay surfaces and interact strongly with the rheology of clays in water mixtures (25−28). Branched PEI was initially used in the present work to reinforce the clay aerogels because of the tendency of linear PEI to crystallize into fibers while cooling in a water solution (29). Branched PEI showed the ability to reinforce the aerogel while retaining the low density desired of the material, increasing the initial compressive modulus to 270 kPa and the density to 0.075 g/cm^3 when 2.5% PEI was incorporated in the starting clay/water mixture. Although these values indicate lower interaction of PEI with clay than PVOH, the molecular weight of the B-PEI was much lower and the initial solution had half the clay loading, leading to the difference in mechanical property values.

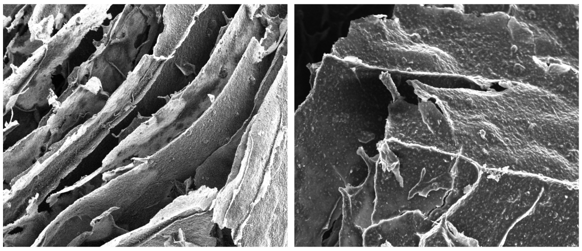

FIGURE 1. Effect of silicification. SEM images showing the PEI/Clay aerogel before (left) and after (right) silicification.

Diatom silicification has been exhaustively studied over the past 50 years providing much information on the process, and has subsequently been mimicked often with similar material. The initial formation of amorphous silica within the organism begins by the uptake of silicic acid and the deposition along silacin protein segments (13−19). Many studies of the deposition of silica on natural and synthetic proteins of this nature have isolated the most easily reproducible segment of the proteins to be a polyamine type subunit (13−21). Being one such type polymer, poly(ethylene imine) has an advantage over other polyamines because, with water present, it exhibits an almost instantaneous silicification directly from alkoxysilanes such as TMOS (20, 29−32). This reaction occurs with a catalytic amount of water that helps in the initial hydrolysis of the alkoxysilane, followed by a condensation into amorphous silica. Because the PEI aerogels in this study are soluble in water, the reaction would necessitate an instantaneous mineralization and prevent the aerogel from deforming.

For silicification of the PEI aerogel to occur, a catalytic amount of water must be present in the aerogel without physically being in water. To prevent too much water uptake, we placed the aerogels in sealed humidity chambers on a platform over LiCl solutions giving relative humidities of 60 and 80%. When kept at 60% RH, the initial modulus only rises from 270 kPa to roughly 870 kPa and upon visual inspection the sample was slightly deformed from its original dimensions. The sample kept at 80% RH and silicified had an initial modulus of roughly 2.8 MPa while maintaining its original dimensions, an increase in modulus of more than 1 order of magnitude. These findings suggest that an ideal catalytic amount of water was present at a relative humidity of 80%.

Further inspection of these materials under SEM shows the aerogel maintains its lamellar structure while adopting a rougher surface on the individual sheets, shown in Figure 1. The silicification changed not only the initial modulus, but the behavior of the aerogel undergoing compression, shown

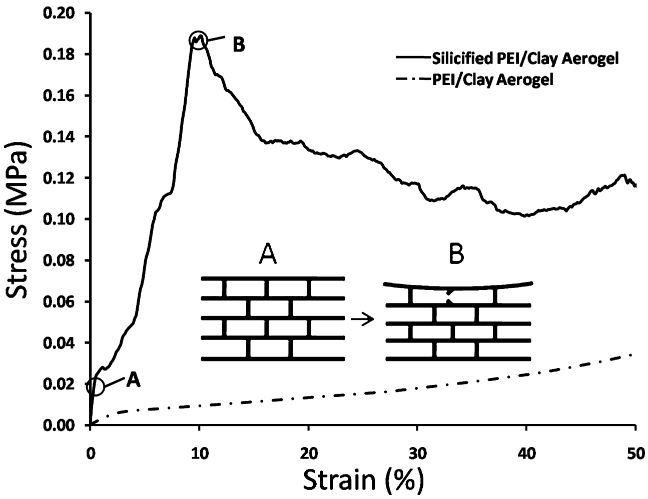

FIGURE 2. Stress−strain behavior of unmodified PEI/clay aerogel (gray) and silicified PEI/clay aerogel (black). The inset visualizes the theoretical behavior of the silicified aerogel in the initial elastic region (A) and the stepwise failure because of brittle ties between layers.

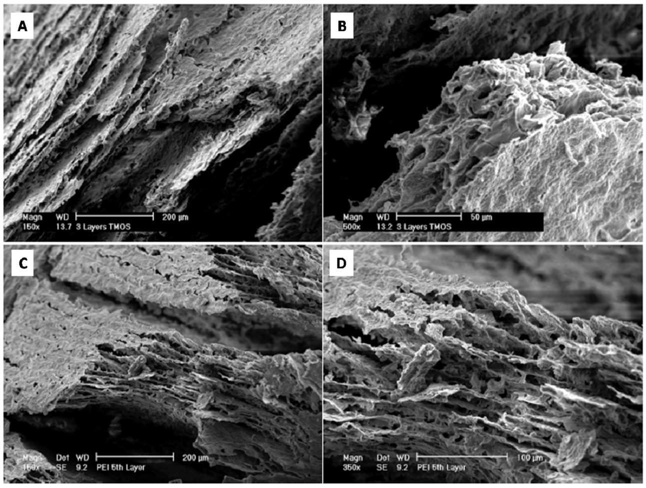

FIGURE 3. Effects of layering on structure. SEM images of silicified aerogels. Different magnifications (A, B) after 3 layers and (C, D) after 5 layers.

in Figure 2. Most clay aerogels tested in compression to date, along with other low density materials such as polymer foams, undergo an initial loading response followed by a leveling off while the material collapses; once all the voids have been collapsed, the stress−strain behavior quickly goes into work hardening (5, 7−9). This behavior is seen in the PEI/PGW aerogel stress strain behavior in compression. After silicification though, the material undergoes a series of localized fractures, avoiding total yield until a critical amount of fractures occurs. This behavior is believed to be because of the increased toughness of the supporting layers along with a decrease in flexibility. Supporting layers can absorb more load, but will undergo brittle fracture one connection at a time.

In many biomineralized systems, such as seashell nacre, additional reinforcement comes not from just a coating of minerals, but a layered system that can absorb and transfer more load through the alternating soft organic phase and hard inorganic phase. This natural approach leads to very tough materials that can withstand much more impact than either material alone through cooperative stress dissipation. Because PEI has such a strong interaction with silicates, an alternative soaking process can be performed where after one silica layer has been deposited, the PEI can be adsorbed to the surface in solution and another layer of silica can be added. For this approach linear PEI was used for enhanced mobility throughout the aerogel (note that the initial aerogel was produced with branched PEI, whereas the subsequent layer additions made use of the linear form of the polymer). Instead of using water, which LPEI can readily crystallize in, methanol was used as the solvent because this crystallization does not occur in methanol. Because of methanol's low vaporization temperature, the LPEI could be assured to stay in the aerogel by flashing the solvent off at 70 °C under vacuum.

Table 1 shows the results of layering up to 5 layers of silica, zero layer indicating the PEI/clay aerogel material before silicification, and Figure 3 shows SEM images of the layering at layer 3 and layer 5 of silica. On the basis of densities of the constituents of these composites, one can calculate that the initial material was composed of approximately 4% solid matter and 96% air; upon repeated silicification, the void fraction of the materials decreases to approximately 85%. Because of small variations in the architecture of each different aerogel, some samples underwent initial yield at various points, many different aspects of the mechanical data were interpreted. The initial modulus is an indication of the material response before any permanent damage is done to the sample and, shown in Figure 4A, the initial modulus of the layered material improved up to the fourth layer of silica, where a small drop was observed. At its highest level of reinforcement with 4 layers of silica, the initial modulus was improved over the original PEI/PGW aerogel by over 20-fold. The secant modulus at 5% was

Table 1. Property Changes Due to the Alternate Layering of PEI and Silica; 0 Layer Indicates Initial, Unmodified PEI/Clay Aerogel

layers	density (g/cm^3)	initial modulus (MPa)	secant modulus at 5% strain (MPa)	toughness at 10% strain (kPa)	toughness at 20% strain (kPa)
0	0.07 ± 0.0	0.23 ± 0.03	0.18 ± 0.04	0.69 ± 0.12	1.8 ± 0.2
1	0.22 ± 0.02	2.8 ± 1.5	1.2 ± 0.3	6.8 ± 1.9	18 ± 5
2	0.23 ± 0.02	3.2 ± 1.0	1.4 ± 0.4	6.6 ± 2.5	21 ± 7
3	0.24 ± 0.03	5.0 ± 2.6	2.0 ± 0.5	9.5 ± 2.3	23 ± 2
4	0.26 ± 0.04	5.0 ± 3.6	2.4 ± 0.0	13.0 ± 1.1	34 ± 3
5	0.28 ± 0.03	4.4 ± 1.8	1.7 ± 0.3	8.9 ± 1.5	36 ± 4

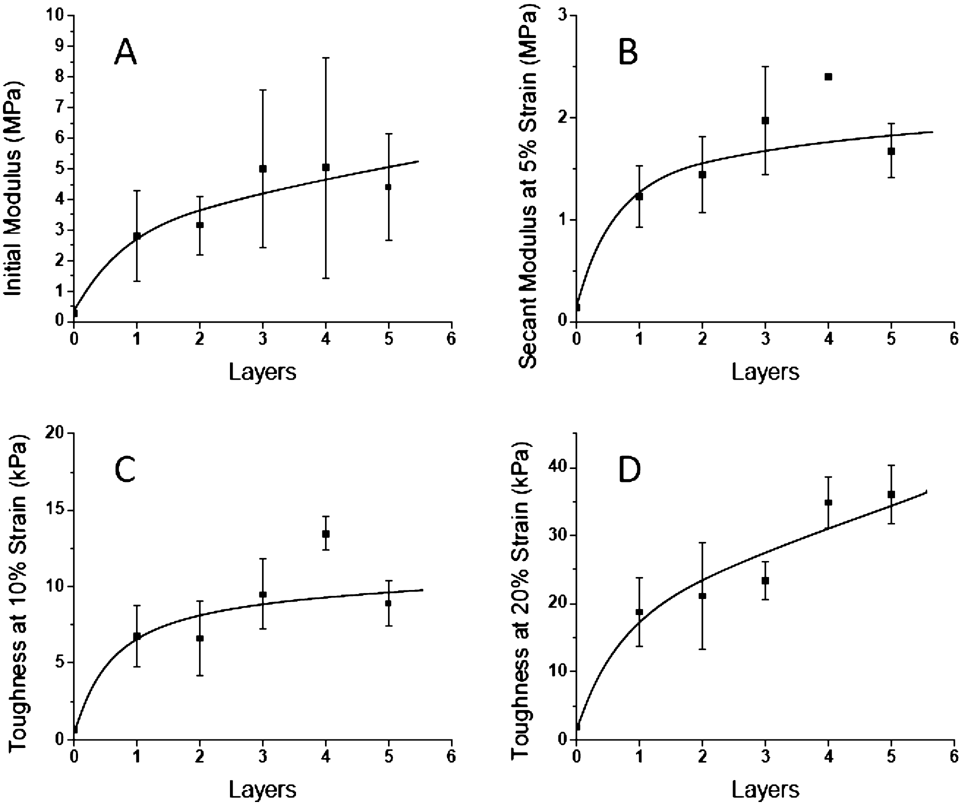

FIGURE 4. Changes in mechanical properties of layered PEI/clay aerogels. Layering silica and PEI shows (A) initial modulus increases, (B) secant modulus increases at 5% strain, and toughness of the material at (C) 10% and (D) 20% strain.

taken as a measure of the materials response after small amounts of permanent damage, where the material would more than likely be used. This measurement followed the same behavior as the initial modulus, with the fourth layer having the highest reinforcement at roughly 20 times higher modulus, shown in Figure 4B. The toughness of the material was calculated as more of an indication as to how well the material would perform, and was calculated at 10 and 20% strain. At 10% strain, the toughness of the material followed the same trend as both modulus values, maxing out in the fourth layer and slightly digressing in the fifth, with the maximum toughness being close to 20-fold higher than the original PEI/PGW aerogel, shown in Figure 4C. At 20% strain the toughness of the fifth layer was the highest, indicating at these high strain values that the material could absorb more load, and was again close to twenty times the original toughness at 20%, shown in Figure 4D. These improvements in each area of mechanical integrity occurred with a minimal increase in the density of the material.

Values in each category of mechanical properties except toughness at 20% seem to indicate a loss in mechanical integrity after 4 layers, but most of the data for the fifth layer of each set lies within the error of the fourth layer, indicating a leveling off of beneficial reinforcement. Further inspection of SEM images of the fifth layer indicate that a layer is forming on the outside of the material which would prevent as much PEI, and therefore silica, from adsorbing inside the material. This behavior would limit the amount of silica buildup and limit the reinforcement of the composite system in general.

CONCLUSIONS

Low density clay aerogels were successfully produced with incorporation of poly(ethylene imine) polymer layers showing marked improvement in compression than clay aerogels of similar clay content. These polymer-modified aerogels provided an effective platform for biomimetic mineralization of silica with tetramethyl orthosilicate, providing silica-encapsulated structures. These materials showed an increase in compressive properties of over 10-fold while still maintaining their structure and low density. Repeated treatment with PEI and orthosilicate resulted in up to five layers of silica/PEI, with progressively enhanced mechanical properties up to 20X better than the unmodified aerogel. As is the case with biomineralized structures that can be found in nature, these synthetic materials exhibit exceedingly high strength:weight ratios, likely resulting from the alternating polymer/inorganic hierarchical structure.

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