Improving the Mechanical Properties of Clay/Polymer Aerogels by a Simple Dip-Coating Procedure

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ABSTRACT: Clay aerogels have many advantages as one of the lowest density family of materials current technology can provide; they possess very low thermal conductivities, high porosities, and high surface areas. Although the mechanical properties of native clay aerogels are rather low, incorporating water-dispersible polymers into the clay gel before they are processed into aerogel forms can easily produce more robust, low-density composites. Various processing modifications and additives can be employed to strengthen the aerogel material, but currently, the materials have some notable weaknesses in abrasion resistance, water absorption, and flexural properties. In this study, we employed a low-cost rubber coating material to quickly and efficiently address all three of these problems. After coating, the aerogels gained significant mechanical reinforcement, a 20-fold increase in flexural modulus and a 15-fold increase in yield stress, while exhibiting an increase of only 8% in the thermal conductivity. Improvements such as these can improve the commercial applicability of clay/polymer aerogels as thermal insulation materials. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: clay; coatings; gels; mechanical properties

INTRODUCTION

Sodium montmorillonite has been used extensively as an inexpensive and nearly inexhaustible reinforcing agent in polymer composites.[1–3] Over the past 10 years, it has also been used as an environmentally friendly source for making aerogel materials.[4–18] The process for producing these aerogel materials is controlled by the freezing of exfoliated clay gels in water with the ice growth confining the clay into grain boundary sheets; this is followed by lyophilization of this frozen material to leave only the "house-of-cards" clay structure behind.[4] These materials are very attractive because of their extremely low densities, low thermal conductivities, high surface areas, and high porosities. With only clay in the suspension, however, these aerogels lack the mechanical properties, solution resistance, and recoverability to make them broadly useful beyond the academic landscape. Many successful attempts to increase the mechanical performance of clay aerogels have been reported recently, with the most widespread success being the incorporation of water-soluble or dispersible polymers in the original water and clay suspension before freeze drying.[5–7,9] Fiber reinforcement has also proven

to be a highly successful way of reinforcing the aerogel composites, with significant improvements in resisting multidirectional stresses.[8] Reactive mixtures have been successful in crosslinking polymers or monomers in the original solution postlyophilizing to impart a great deal of recovery; this makes these materials behave much like polymer foams.[5,7] Even more recently, there have been efforts to develop silica layers on the surface of the clay/polymer composites that can increase the mechanical values by a factor of 10.[11] It has been shown that these reinforcement methods will slightly increase the density of the aerogels while still retaining a very low thermal conductivity; this makes these materials very attractive as more ecofriendly replacements for traditional polymer foams.

Thermal conductivity aside, another reasons that clay aerogels are inherently important is the ease in which the aerogels can be molded into any shape desired. The clay gel freezes to the shape of whatever container it is in; this gives the materials a distinct advantage over materials that need to be shaped into their desired part after formation. The lateral and vertical orientations of the structural layers in clay aerogels have previously been studied in detail.[16] The results of these studies show higher strength in the oriented direction, but without further modification, the aerogel can be weak in the layer perpendicular to orientation. Coating technology, in all various forms, is one of the principle

applications in polymer science. We hoped to use the application of coating technology to aerogel technology to address the problems posed by the vertical orientation by adding a flexible outer layer to give the material flexural stability and abrasion resistance while minimally affecting the density of the aerogel.

EXPERIMENTAL

Materials

Sodium montmorillonite (PGW grade) was obtained from Nanocor, Inc. (Hoffman Estates, IL), and was used as received. Deionized water was obtained with a Barnstead Nanopure low-pressure, reverse-osmosis purification system. Triethylenetetraamine and 1,4-butantediol diglycidyl ether were obtained from Sigma Aldrich Co. and were used as received. Liquid Tape, made by Performix, a dispersion of synthetic rubber in organic solvent, was purchased from a local vendor and was used as received. A Urethane RTV Mold-Making System was obtained from TAP Plastics and was used as received. The aerogel sample for thermal conductivity measurements was provided by Aeroclay, Inc., and was produced from 5% clay, 2.5% polyvinyl alcohol (PVOH), and 1% poly(vinyl alcohol) fibers in the original aqueous mixture before freeze drying.

Materials and preparation of the polymer/clay solutions

1,4-Butantediol diglycidyl ether (16.115 g) was added to 100 mL of deionized H_2O and mixed thoroughly by hand until it was dissolved. Sodium montmorillonite (5.000 g) was mixed in slowly with an electric hand mixer, and we were careful to avoid bubble formation. Triethylenetetraamine (3.885 g) was added slowly and mixed in thoroughly by hand. The samples were transferred directly to freeze-drying molds, which were transferred immediately to a Vir-Tis AdVantage@ EL-85 freeze dryer. The shelf was cooled down to $-30^{\circ}C$ until the samples were completely frozen; then, they were freeze-dried for 96 h. After freeze drying, the samples were placed in a vacuum oven at $80^{\circ}C$ for 24 h to complete the curing reaction.

Coating

The samples were cut into the desired shape for testing with a band saw when needed. Copper wire was pushed through the sample to hold it during coating. The samples were then dip-coated with the rubber dispersion and hung to dry. Any holes from removing the copper wire were sealed afterward with an additional spot coating of the exposed areas with a brush. The panel providing for the thermal conductivity measurements was coated by a brush and left to dry overnight.

Testing

All samples were measured and weighed to obtain densities before and after coating. Mechanical testing (ASTM D 3575) was conducted with an Instron model 5500 universal testing machine equipped with a 1-kN 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. Flexural testing bars were created with a custom mold to give samples with a width and height of approximately 11 mm and a span of 127 mm. Cube samples were 20 mm in each direction. All data analysis was performed in Microsoft Excel. Thermal analysis testing was performed with a LaserComp Fox 314 heat flow meter.

RESULTS AND DISCUSSION

In initial studies to form the clay aerogels, we found that a concentration of 5 wt % solids in the initial solution gave densities close to 0.05 g/cm^3 and a compressive modulus of approximately 10 kPa.[12] Although that density was very low, the associated mechanical properties were far too low to be of significant value by this method alone. Attempts to increase the mechanical values have been exhaustive and have most commonly employed the use of a water-soluble polymer with some sort of interaction with clay to get the best results while keeping the density low. Poly(vinyl alcohol) has been one of the most studied systems to date and can lend much mechanical improvement while still providing very low densities and thermal conductivities.[16] With a 5 wt % addition of poly(vinyl alcohol) at a weight-average molecular weight of 85,000–124,000 g/mol, for example, the initial compressive modulus rose more than two orders of magnitude relative to the that of the pure clay aerogels to 1.6 MPa.[17] The inclusion of natural and synthetic fibers has also pushed the boundaries of mechanical robustness by acting as a reinforcement for the system and transferring load to the continuous fiber to lower the stresses on the individual clay/polymer sheets.[8]

Most aerogels reinforced only by water-soluble polymers gain a significant amount of mechanical integrity with a higher addition of polymer but only become useful materials with around 2.5–5 wt % addition. A 20 wt % addition of the epoxy starting material was needed to increase the initial modulus to about 0.5 MPa, which was slightly lower than a 5 wt % addition of poly(vinyl alcohol) ($\sim$ 1.5 MPa) but with much more starting material. The density
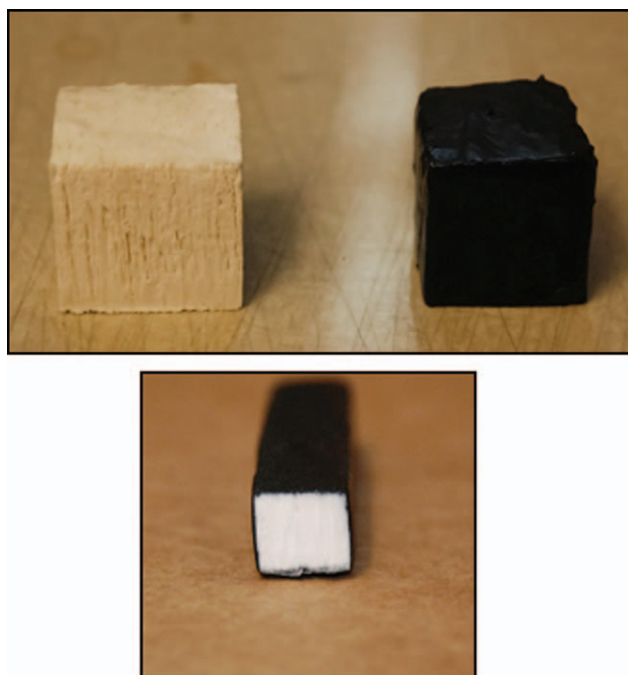
Figure 1 Aerogels with coatings applied. The top images show the cube-shaped aerogel sample before and after coating. The bottom image shows a cross section of the material after coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in that system rose to 0.2 g/cm^3, which was close to that of similar composites and still relatively low. The main advantage of using the epoxy system was the ability to crosslink, which made the aerogels insoluble in water. With such high crosslink density, the elasticity and recovery of the aerogel were found to be much higher than that obtained with normal methods of reinforcement.
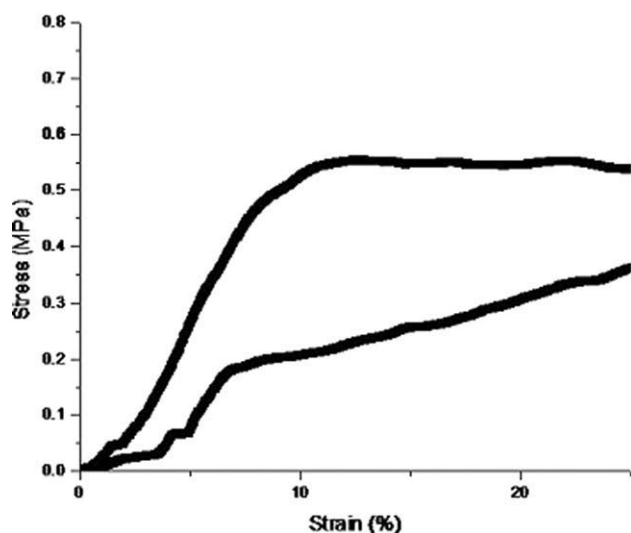
To further improve this technology, it is important that the material coating the aerogels be tough, easily obtainable, and low in cost. A commercially available synthetic rubber coating material was chosen because it met the performance requirements while also possessing a rapid drying time and ease of application. Epoxy aerogel samples were dip-coated and dried overnight; this produced relatively uniform coatings of about 0.38 mm in all of the samples, as measured with a digital caliper. Samples before and after coating and a cross section of the coating on the aerogel are shown in Figure 1. The samples were cube shaped for compression testing and rectangular for flexural testing.

The initial properties of the coated aerogels were vastly improved compared with those of the uncoated original materials. The average density of the cube-shaped aerogel samples rose from 0.22 to 0.35 g/cm^3, while the smaller flex bar density rose from 0.24 to 0.39 g/cm^3. Because these were smaller samples and the average coating thickness of all of the samples was fairly uniform at 0.38 mm, we could assume that the density changes would be less important with larger samples. Compression testing was then performed to evaluate the practical improvements that the coating offered. Shown in Figure 2 are common stress–strain curves for the coated material compared to the original epoxy aerogel; this figure shows a marked improvement in all aspects of the mechanical performance. Figure 3 shows that the initial modulus rose from 0.41 MPa in this specific sample set to 1.6 MPa. Because the initial modulus can have large variations from sample to sample, with these materials, a better indication of performance during use may be the working modulus, which is measured after the initial

Figure 2 Compression behavior for the epoxy aerogel with coating (top) and without coating (bottom).
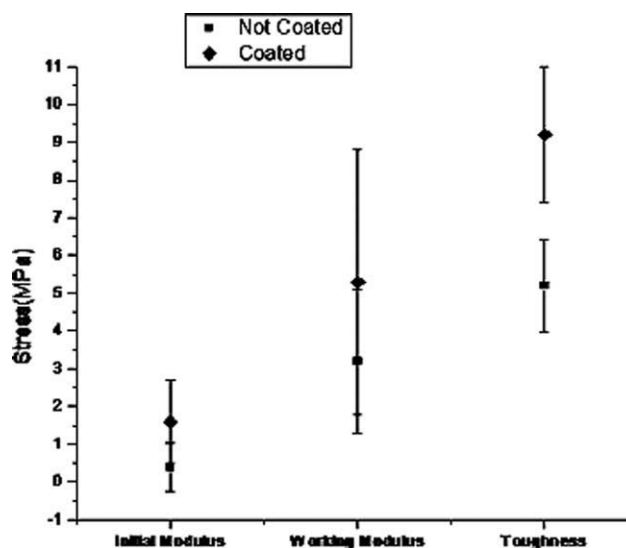

Figure 3 Mechanical properties for the epoxy aerogels before and after coating.
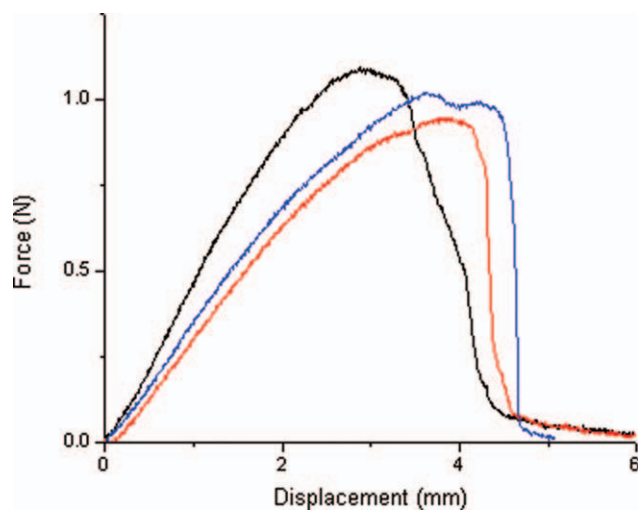
Figure 4 Force–displacement curves for the flexural testing of the epoxy aerogels (three replicate samples). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
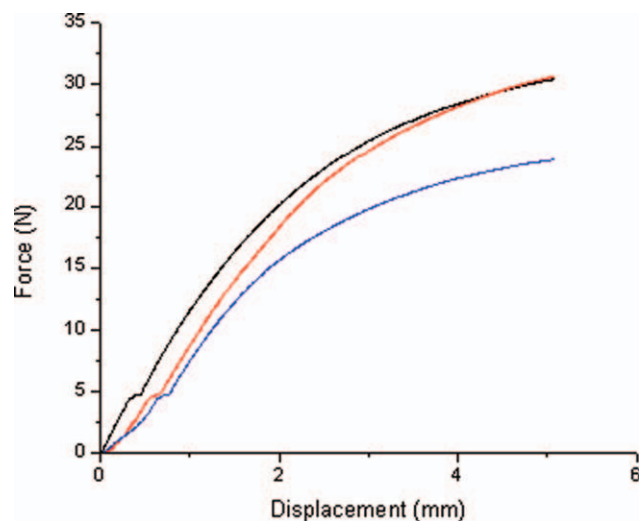
Figure 5 Force–displacement curves for the flexural testing of the coated epoxy aerogels (three replicate samples). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
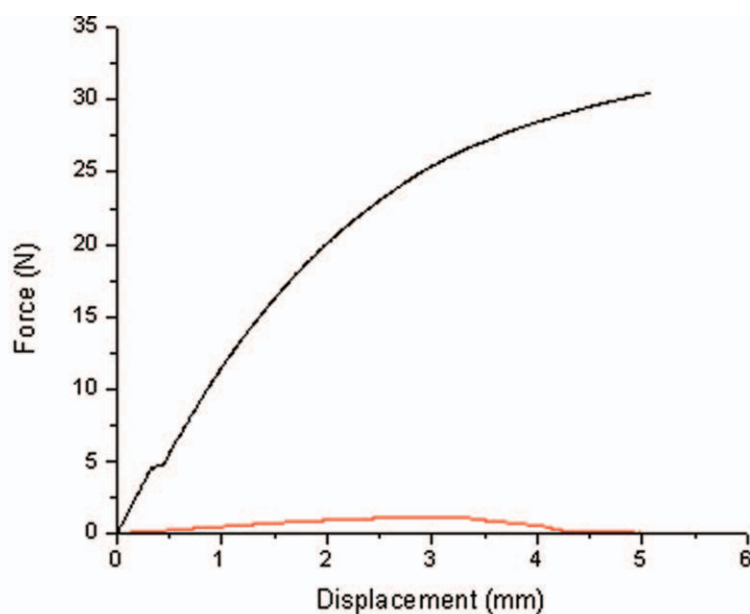
Figure 6 Comparison of the mechanical behavior before and after coating (top) with an image of complete failure without coating (bottom). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modulus and within the elastic region of deformation. The working modulus rose from 3.2 MPa in the original epoxy aerogel to 6.4 MPa in the coated materials, an increase by a factor of two. The toughness values almost doubled as well with coating, rising from 5.2 to 9.2 MPa. Overall, the enhancement in the mechanical values in compression rose somewhat with a small application of the coating layer on the outside of the material, although it should be noted that there were some overlaps in the data presented in Figure 3. It should be pointed out as well that the coated poly(vinyl alcohol) or epoxy aerogel samples exhibited no apparent loss in properties when they were placed in water.

Flexural testing of unreinforced clay aerogels is somewhat difficult, as samples tend to break at relatively low strains because of weak cohesion between the layers of the material. That behavior was indeed the case with the epoxy aerogels, shown in Figure 4; the samples broke cleanly at low levels of displacement. This type of behavior is a severe limiting factor in aerogel applications, as even in low-flexure applications such as thermal insulation, these materials still need to have some flexural integrity. By coating the aerogels with a synthetic rubber layer, the samples not only gained mechanical performance, but the coating prevented the samples from breaking. The data from these experiments are shown in Figure 5. Figure 6 shows a comparison of the flexural testing between the two samples with an image showing the samples after testing. The coated samples outperformed the original aerogels, with the flexural modulus increased from 0.82 MPa in the original epoxy aerogels to 17 MPa in the coated material. The yield strength of the coated aerogels similarly increased from 0.95 to 15 N; this reflected an increase of more than an order of magnitude in the mechanical properties over the initial, uncoated aerogels.

The coated aerogel can be considered to be a classic sandwich composite, with the rubber coating reinforcing the aerogel material, specifically in flexure, to retain low density while increasing the use of such a material. Gibson and Ashby[18] expounded on the theory and optimization of such a structure, in particular, to a coating being applied to a foam core.

When the mechanical properties are measured in flexure, one common property in coated foams is the equivalent flexural rigidity (R_{eq}), which can be obtained by the following equation[18]:

$$E_{tot}I = \frac{E_f b t^3}{6} + \frac{E_c b c^3}{12} + \frac{E_f b t d^2}{2} = R_{eq}$$

where R_{eq} is the equivalent flexural rigidty, E_{tot} is the flexural modulus of the coated composite, I is the second moment of inertia, E_f is the flexural modulus of the coating/face, E_c is the flexural modulus of the core, b is the width of the coated material, t is the thickness of the coating, c is the core thickness, and d is the total sample thickness. The first term accounts for the contributions of the coating, the second term accounts for contributions from the core, and the third term accounts for the contributions of the coating to the whole sample. When this method is used to solve for the modulus of the rubber coating, the expression is reduced to $E_f \approx 92$ MPa. When compared to the core flexural modulus and composite flexural modulus ($E_c = 0.82$ MPa, $E_{tot} = 17$ MPa), it becomes apparent that the coating significantly reinforces the material.

A significant increase in the mechanical properties has been fully demonstrated for aerogels coated with a synthetic rubber material, but this advantage can come with some trade-offs, mainly in the thermal conductivity. If the thermal conductivity for the coating is much higher than that of the aerogel, which, given the very low thermal conductivity of aerogels, is assumed to be the case, conductive thermal transfer could occur throughout the coating and short circuit the aerogel's insulative structure. Because the coatings used in this study were very thin in relation to the aerogel samples, this conductive concern might not have been problematic, but it needed to be tested. For this experiment, an external sample was received from Aeroclay, Inc., with known thermal conductivity values, which were very low for good comparison. The thermal conductivity values for the original and coated samples are given in Table I. It is clear that the thermal conductivity did increase but not by an appreciable amount, and these coated materials were well in the range of other low-thermal-conductivity insulators.

CONCLUSIONS

Through a study with a common coating material, a method was established for coating aerogel materials with a thin uniform coating. Coating the materials with this specific synthetic rubber coating gave significant increases in the aerogel material performance, most importantly in the flexural properties, in which there was a 20-fold increase in the flexural modulus and a 15-fold increase in the yield stress. With this

coating, the flexural performance of aerogel materials could compete with more traditional insulating materials, such as glass fiber/epoxy or polymer foams. The thermal properties did not change significantly with this coating, only increasing by 8% of the original aerogel; the water sensitivity of the aerogels were effectively eliminated as well, so this technology would be highly advantageous to aerogel applications in insulation and other applications. It can be assumed that other coatings with different chemistries could impart characteristics such as selective absorption, hydrophobicity/oliophobicity, and tailored mechanical reinforcement.

References

1. Grim, R. E. Clay Mineralogy; McGraw-Hill: New York, 1953.
2. Pinnavaia, T. J.; Beall, G. W. Polymer–Clay Nanocomposites; Wiley: Chichester, England, New York, 2000.
3. Lu, G. Q.; Zeng, Q. H.; Yu, A. B.; Paul, D. R. J Nanosci Nanotechnol 2005, 5, 1574.
4. Somlai, L. S.; Bandi, S. A.; Schiraldi, D. A.; Mathias, L. J. AIChE J 2006, 52, 1162.
5. Bandi, S.; Bell, M.; Schiraldi, D. A. Macromolecules 2005, 38, 9216.
6. Bandi, S.; Schiraldi, D. A. Macromolecules 2006, 39, 6537.
7. Arndt, E. M.; Gawryla, M. D.; Schiraldi, D. A. J Mater Chem 2007, 17, 3525.
8. Finlay, K.; Gawryla, M. D.; Schiraldi, D. A. Ind Eng Chem Res 2008, 47, 615.
9. Gawryla, M. D.; Nezamzadeh, M.; Schiraldi, D. A. Green Chem 2008, 10, 1078.
10. Schiraldi, D. A.; Gawryla, M. D.; Bandi, S. A. U.S. Pat. Appl. 20070208124 (2007).
11. Johnson, J. R.; Spikowski, J.; Schiraldi, D. A. Am Chem Soc Appl Mater Interfaces 2009, 1, 1305.
12. Alhassan, S. M.; Qutubuddin, S.; Schiraldi, D. A. Langmuir 2010, 26, 12198.
13. Gawryla, M. D.; Schiraldi, D. A. Macromol Mater Eng 2009, 294, 570.
14. Pojanavaraphan, T.; Liu, L.; Ceylan, D.; Okay, O.; Magaraphan, R.; Schiraldi, D. A. Macromolecules 2011, 44, 923.
15. Pojanavaraphan, T.; Magaraphan, R.; Chiou, B. S.; Schiraldi, D. A. Biomacromolecules 2010, 11, 2640.
16. Abramson, A. R.; Hostler, S. R.; Gawryla, M. D.; Bandi, S. A.; Schiraldi, D. A. Int J Heat Mass Transfer 2009, 52, 665.
17. Lamison, K.; Gawryla, M. D.; Schiraldi, D. A. Abs Pap Am Chem Soc 2007, 233.
18. Gibson, L. J.; Ashby, M. F. Cellular Solids: Structure and Properties; Pergamon: Oxford, 1988.