Clay Nanocomposite/Aerogel Sandwich Structures for Cryotanks

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Abstract

GRC research has led to the development of epoxy-clay nanocomposites with 60-70% lower gas permeability than the base epoxy resin. Filament wound carbon fiber reinforced tanks made with this nanocomposite had a five-fold lower helium leak rate than the corresponding tanks made without clay. More recent work has produced new composites with more than a 100-fold reduction in helium permeability. Use of these advanced, high barrier composites would eliminate the need for a liner in composite cryotanks, thereby simplifying construction and reducing propellant leakage.

Aerogels are attractive materials for use as cryotank insulation because of their low density and low thermal conductivity. However, aerogels are fragile and have poor environmental stability, which have limited their use to certain applications in specialized environments (e.g., in certain types of nuclear reactors as Cerenkov radiation detectors, and as thermal insulators aboard space rovers on Mars). New GRC developed polymer crosslinked aerogels (X-Aerogels) retain the low density of conventional aerogels, but they demonstrate a 300-fold increase in their mechanical strength. Currently, our strongest materials combine a density of ~0.45 g/cc, a thermal conductivity of ~0.04 W/mK and a compressive strength of ~185 MPa. Use of these novel aerogels as insulation materials/structural components in combination with the low permeability of epoxy-clay nanocomposites could significantly reduce cryotank weight and improve durability.

Introduction

Previous efforts to reduce cryotank weight through the use of composite materials in place of traditional metals have had limited success. Concerns about the permeability and damage tolerance of cryotanks have led to the over design of composite tanks which adds weight and negates any benefits that might be realized by the use of lightweight composite materials. Full utilization of composite materials requires the development of new lightweight, thermally insulating, mechanically robust composite sandwich structures with low permeability and good resistance to microcracking as well as good damage tolerance to withstand any impact damage during servicing, fueling, launch or deployment.

Traditionally, metallic tanks have been used for housing cryogenic fluids. The advantages of such tanks include high strength and stiffness, and low permeability. Presently, it appears that the replacement of traditional metallic cryogenic fuel tanks with polymer matrix composite (PMC) tanks may lead to significant weight reductions and hence increase load carrying capabilities.[1] However, the tanks must be able to withstand flight loads and temperatures ranging from -250 ^{o}C to 120°C, without loss of cryogenic fuel due to microcracking or delamination.

A critical concern with composite materials is matrix microcracking at cryogenic temperatures.[2] Microcracking allows permeation of the cryogenic fluid into the bulk polymer matrix which can result in catastrophic failure. For composite tanks to be a viable replacement to the current tanks, an approach must be taken which reduces permeability of the composite but also enhances the strength and toughness of the composite matrix.

Several approaches have been taken to design lightweight composite sandwich structures for cryotank construction. Many designs incorporate a metallic or polymeric liner, where the liner material has low gas permeability.[3,4] While some of these approaches have been successful, there remains the issue of the added weight of the liner, CTE mismatch, and propellant permeation. For example, significant core/face sheet delaminations in these sandwich structures were observed in the failure of the X-33 Liquid Hydrogen Tank.[5]

While previous efforts have relied on the use of conventional composite and core materials to reduce the microcracking and permeability of the tanks, advances in nanotechnology derived materials may enable the production of ultra-lightweight cryotanks with significantly enhanced durability and damage tolerance. Layered silicate nanocomposites are attractive materials for composite cryogenic storage tanks. These materials often exhibit an order of magnitude reduction in gas permeability when compared to the base resin. In addition, polymer-silicate nanocomposites have been shown to yield improved material strength and modulus, with minimal negative impact on toughness.[6]

Similarly, molecular manipulation of the delicate framework of a silica aerogel consisting of a three dimensional structure of nanoparticles (1-10 nm across) allows a desirable combination of macroscopic properties such as high strength and low density.[7-9] Specifically, by tailoring the surface chemistry of silica we can build molecular oligomeric tethers between the skeletal nanoparticles of the aerogel leaving the void space between the nanoparticles open. That results in a dramatic increase in the specific strength of the material at a minimal increase in density. Thus the low thermal

conductivity of the native silica aerogel is retained and the new material (X-Aerogel) can now play the dual role of the thermal insulator/structural component of a cryogenic tank, eliminating the need for metal.

Experimental

The resins chosen were Epon 826 with D230 curing agent, and Epon 862 with W curing agent. These are not toughened resins, but were chosen because previous work has shown good silicate dispersion in these matrices. Therefore, the added effects of the silicate were of interest, rather than resin properties. Toughened epoxy nanocomposites are currently being prepared and analyzed.

Materials

Epon Resins (826 and 862) and the W curing agent were donated by Resolution Performance Products. Huntsman Chemical Company generously supplied the Jeffamine D230 curing agent. Organically modified clays were received from Southern Clay Products (Closite 30B) and from Professor Tom Pinnavaia's group at Michigan State University (ODA-clay).

Nanocomposite Synthesis

Epoxy-clay nanocomposite plaques (4"x4") were prepared by stirring the epoxy (15g) with either 0 wt%, 2 wt% or 5 wt% organically modified silicate on a hotplate. The temperature was set so that the epoxy viscosity was reduced and stirring with a magnetic stir bar was possible. The epoxy portion was cooled and the crosslinking agent was added (5.25g). The mixture was poured into a 4"x4" mold and degassed at $60^{\circ}C$ for 3

hours under vacuum. The resin was then cured in an air-circulating oven by heating at 75°C for 2 hours and 125°C for 2 hours.

Characterization

X-ray diffraction (XRD) patterns were obtained using a Philips XRG 3100 X-ray diffractometer with Ni-filtered CuKα radiation. Transmission electron microscopy (TEM) specimens were prepared by microtoming sections of the nanocomposites, 70 to 80 nm thick, and floating the sections onto Cu grids. Micrographs were obtained with a Philips CM 200, using an acceleration voltage of 200 kV.

CTE measurements were made using a TA instruments ThermoMechanical Analyzer. The Izod Impact data was collected on a Custon Scientific Instruments Inc. Impact tests were according to ASTM D256, Test C, Notched specimens, using a 6 in-lb weight source.

Helium Permeability measurements were performed by Ms. Sofia Martinez of Professor David Hui's group at the University of New Orleans.

Results and Discussion

The significant enhancements in barrier performance that are typically reported for clay nanocomposites are dependent on the level of silicate separation. A high level of dispersion creates a maximum path length for the permeating gas, thereby slowing gas diffusion. In most samples, wide angle XRD did show a peak corresponding to an expanded d_{001} spacing of the silicate layers, as well as a reduction in peak intensity. This suggests a combined intercalated and exfoliated nanocomposite morphology, which was

supported by TEM. Figure 1 illustrates both the intercalated and exfoliated regions of the 826/ 5% ODA clay nanocomposite.
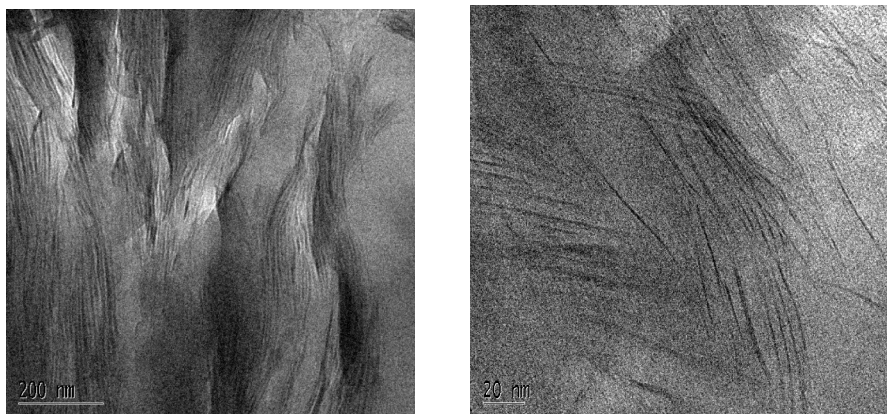

Figure 1: TEM images of (a) intercalated nanocomposite morphology and (b) exfoliated nanocomposite morphology.

Permeability measurements

The addition of either Closite 30B or ODA to Epon 862 resulted in up to a 67% decrease in permeability compared to the base resin, as shown in Figure 2. Reductions in permeability between 30 and 80% are often observed for clay nanocomposites. This is due to the random arrangement of the clay layers, which increases the path of the diffusing gas. However, because the layers are not oriented, the increase in path length is not maximized. It has been assumed that orienting the clay layers within the bulk resin would yield the lowest permeability and there is some indication that carbon fiber reinforcement of layered silicate nanocomposites may result in alignment of the silicate along the fiber axis.[10] Results of leak rate tests on a 9L, carbon fiber reinforced, nanocomposite tank prepared at GRC support this. The nanocomposite matrix tank

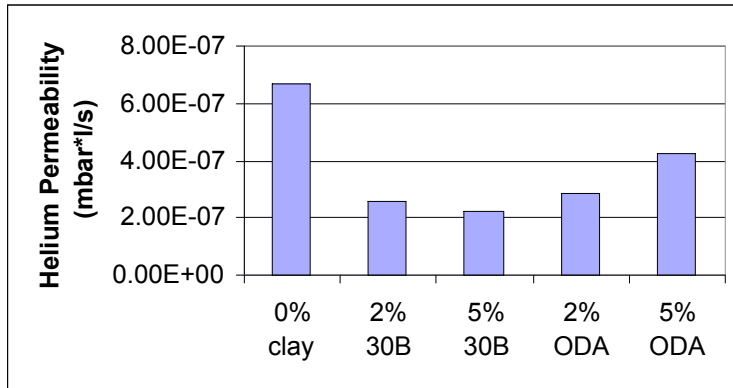showed a 5-fold reduction in helium leak rate compared to the carbon fiber reinforced neat resin tank.

Figure 2: Decrease in helium permeability as a result of silicate dispersion.

The permeability of the Epon 826 resins is currently being evaluated.

CTE: The coefficient of thermal expansion is an important parameter to consider when developing materials for cryogenic tanks. The primary cause of microcracking is the difference in the CTE of the matrix and the reinforcing carbon fibers. Layered silicates have been reported to lower the CTE of the matrix[11] and evaluation of the nanocomposites prepared in this study show a modest decrease. The results for CTE measurements below the resin T_g are listed in Table 1.

EPON 826	CTE ($\mu m/^oC$)	EPON 862	CTE ($\mu m/^oC$)
0% silicate	83 +/- 5	0% silicate	84 +/- 10
2% ODA	60 +/- 4	2% ODA	57 +/- 9
5% ODA	60 +/- 11	5% ODA	63 +/- 0
2% 30B	70 +/- 10	2% 30B	64 +/- 6
5% 30B	75 +/- 0	5% 30B	67 +/- 6

Table 1: CTE measurements for epoxy resins and nanocomposites.

On average, the resin CTE was lowered by 25% when clay was added. A decrease in CTE of the nanocomposite can be attributed to the fine dispersion and rigidity of the clay

platelets in the epoxy matrix, which can inhibit the expansion of polymer chains as the temperature is raised.[12]

Toughness: Impact testing has shown that addition of silicate to these resins reduced the toughness when compared to the base resin. This has been observed in other systems where a rigid filler was added to a polymeric matrix. In this case however, the decrease was minimal. Table 2 lists the notched impact results

EPON 826	Impact Resistance (J/m)	EPON 862	Impact Resistance (J/m)
0% silicate	25 $^+$/- 1	0% silicate	14 $^+$/- 4
2% ODA	17 $^+$/- 1	2% ODA	13 $^+$/- 1
5% ODA	14 $^+$/- 1	5% ODA	13 $^+$/- 1
2% 30B	19 $^+$/- 2	2% 30B	10 $^+$/- 2
5% 30B	15 $^+$/- 2	5% 30B	10 $^+$/- 2

Aerogels:

A typical X-Aerogel can be made by co-gelation of tetramethoxysilane (TMOS) with aminopropyltriethoxysilane (APTES) yielding a nanostructured gel whose internal surfaces are rich with amines.[7-9] Subsequently, the nanoparticles are bonded together with a conformal coating of polyurea that results from the reaction of a di-isocyanate with the surface amines. Removal of the pore filling solvent under supercritical conditions results in strong lightweight X-Aerogels. The most dense samples (ρ~0.48 g/cc) rely on a native silica framework with bulk density of ~0.20 g/cc, have a thermal conductivity of ~0.04 W/mK and a compressive strength of ~185 MPa and a Young's modulus of ~130 MPa. A typical stress-strain curve is shown in Figure 3 (Data provided by Prof. Samit Roy of Oklahoma State University).
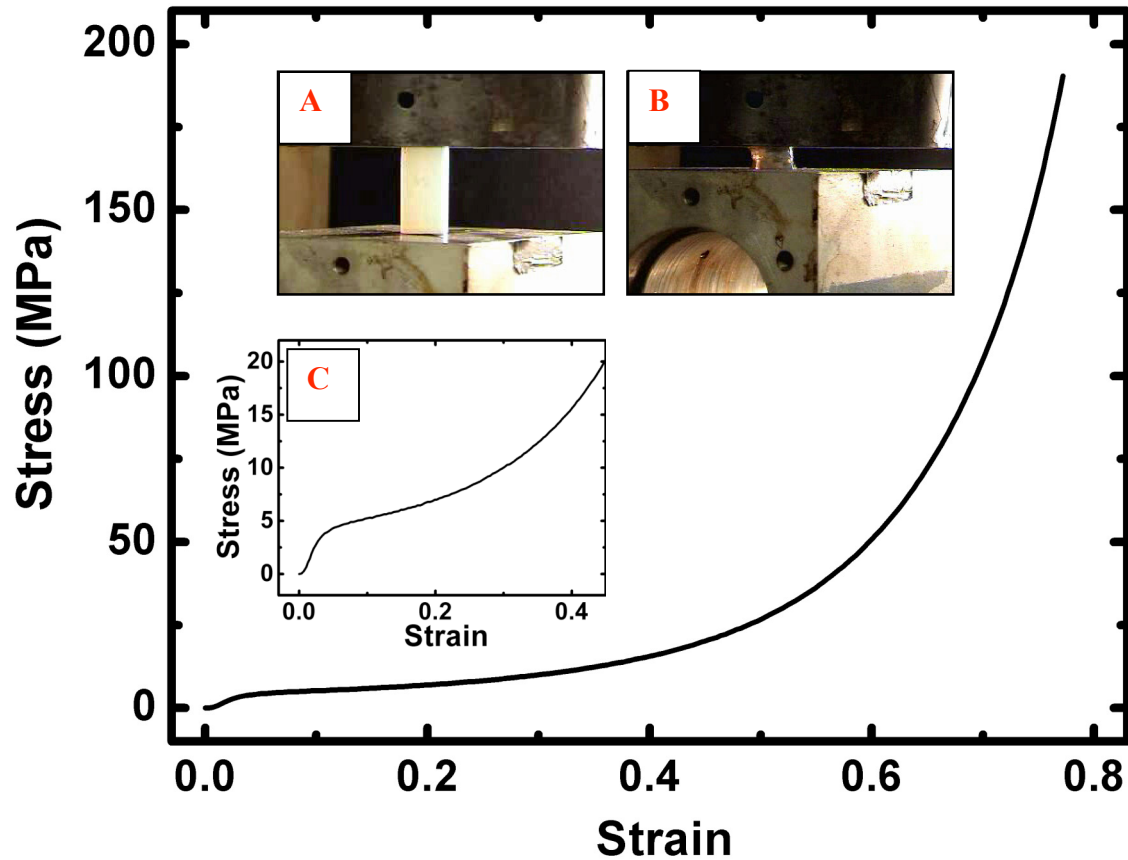
Figure Caption. Mechanical compression testing of a Desmodour N3200 crosslinked APTES-modified silica aerogel cylinder ~0.5" diameter, ~1" long. <u>Inset A</u>: The set up before testing; <u>Inset B</u>: The set up at the point of collapse; <u>Inset C</u>: Expanded low strain range.

Conclusions

Dispersion of layered silicate clays in two separate epoxy matrices showed a reduction in both resin permeability and CTE. The resin toughness was also reduced. However, these results, as well as preliminary data from the composite tank, suggest that

nanocomposite materials may be a viable route to the preparation of linerless composite tanks.

References

1. T.S Gates, K.S. Whitley, R.W. Grenoble and T. Bandorawalla, "Thermal/ mechanical durability of polymer-matrix composites in cryogenic environments", *44th AIAA Conference*, April 7-10, AIAA 2003-1600.

2. J. Humpenoder, "Gas permeation of fibre reinforced plastics", *Cryogenics*, **38**(1), (1998) 143-147.

3. B.W. Grimsley, R.J. Cano, N.J. Johnston, A.C. Loos, and W.M. McMahon, "Hybrid composites for LH2 fuel tank structure", *NASA technical report*, 2001.

4. J.M. Lifshitz and H. Dayan, "Filament-wound pressure vessel with thick metal liner", *Composite Structures*, **32** (1995) 313-323.

5. M.J. Robinson, J.D. Eichinger and S.E. Johnson, "Hydrogen permeability requirements and testing for reusable launch vehicle tanks", *43rd AIAA Conference*, April 22-25, AIAA 2002-1418.

6. D. Schmidt, D. Shah and E.P. Giannelis, "New advances in polymer/ layered silicate nanocomposites", *Current Opin. Solid State and Mat Sci*, **6** (2002) 205-212.

7. (a) M. A. B. Meador, E. F. Fabrizio, F. Ilhan, A. Dass, G. Zhang, P. Vassilaras, J. C. Johnston, N. Leventis "Crosslinking Amine-Modified Silica Aerogels with Epoxies: Mechanically Strong Lightweight Porous Materials," *Chem. Mater.* **2005**, *17*, 1085-1098. (b) G. Zhang, A. Dass, A.-M. M. Rawashdeh, J. Thomas, J. A. Counsil, C. Sotiriou-Leventis, E. F. Fabrizio, F. Ilhan, P. Vassilaras, D. A. Scheiman, L. McCorkle, A. Palczer, J. C. Johnston, M. A.

B. Meador, N. Leventis "Isocyanate Cross-Linked Silica Aerogel Monoliths: Preparation and Characterization," *J. Non-Cryst. Solids* **2004**, *350*, 152-164. (c) J. F. Hund, M. F. Bertino, G. Zhang, C. Sotiriou-Leventis, N. Leventis "Synthesis of Homogeneous Metal Alloy Clusters in Silica Aerogels," *J. Non-Cryst. Solids* 2004, *350*, 9-13. (d) M. F. Bertino, R. R. Gadipalli, J. G. Story, C. G. Williams, G. Zhang, C. Sotiriou-Leventis, A. T. Tokuhiro, S. Guha, N. Leventis "Laser Writing of Semiconductor Quantum Dots in Silica Aerogels," *Appl. Phys. Lett.* **2004**, *85*, 6007-6009. (e) M. F. Bertino, J. F. Hund, G. Zhang, C. Sotiriou-Leventis, A. T. Tokuhiro, N. Leventis "Room Temperature Synthesis of Noble Metal Clusters in the Mesopores of Mechanically Strong Silica-Polymer Aerogel Composites," *J. Sol-Gel Sci. Tech.* **2004**, (in press). (f) N. Leventis, A.-M. M. Rawashdeh, I. A. Elder, J. Yang, A. Dass and C. Sotiriou-Leventis "Synthesis and Characterization of Ru(II) Tris(1,10-phenanthroline)-Electron Acceptor Dyads Incorporating the 4-benzoyl-*N*-methylpyridinium cation or *N*-Benzyl-*N´*-methyl-viologen. Improving the Dynamic Range, Sensitivity and Response Time of Sol-Gel Based Optical Oxygen Sensors," *Chem. Mater.* **2004**, *16*, 1493-1506.

8. M. F. Bertino, J. F. Hund, J. Sosa, G. Zhang, C. Sotiriou-Leventis, N. Leventis, A. Tokuhiro and J. Terry "High Resolution Patterning of Silica Aerogels," *J. Non-Cryst. Solids* **2004**, *333*, 108-110.

9. G. Zhang, A.-M. M. Rawashdeh, C. Sotiriou-Leventis, N. Leventis "Isocyanate Cross-Linked Silica: Structurally Strong Aerogels," *Polymer Preprints* **2003**, *44(1)*, 35-36.

10. J.F. Timmerman, B.S. Hayes and J.C. Serefis, "Nanoclay reinforcement effects on the cryogenic microcracking of carbon fiber/ epoxy composites", *Composites Sci and Tech*, **62** (2002) 1249-1258.

11. H.L. Tyan, C.Y. Wu and K.H. Wei, "Thermal and moisture absorption properties of polyimide of different chemical structures", *J. Appl. Poly. Sci*. **81** (2001) 1742-1747.

12. A. Yasmin, and I.M. Daniel, "Mechanical and thermal properties of graphite platelet/ epoxy composites", *Polymer* **45** (2004) 8211-8219.