

Hierarchical carbon nanotube-alumina oxide fiber reinforced composites and oxide hydration kinetics

Ajay Krishnamurthy^{1,2}, Alexis Brake³, Andrew Liotta⁴, Brian Wardle⁴, Aaron M. Forster²

¹Theiss Research, La Jolla, CA 92037, USA

²Material Measurement Laboratory and ³NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

³University of Florida, Gainesville, FL 32611, USA

⁴Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, MA 02139, USA
aaron.forster@nist.gov

Introduction

Directly growing carbon nanotubes (CNTs) from fiber surfaces has added new capabilities to traditional fiber reinforced polymer composites (FRP), making them electrically and thermally conductive while improving their resistance to shear failure. The durability of these materials is not well understood. Ceramic alumina microfibers serve as a model platform for studying the mechanical, electrical, and thermal properties of fibers modified using CNTs. These hierarchical FRPs utilize the chemical vapor deposition (CVD) process to grow dense, highly aligned forests of CNTs from the fiber surfaces. The alumina fibers are available in similar weaves used for glass and carbon reinforcements, in addition they can withstand the chemical vapor deposition process with no loss in mechanical strength of the fibers. In traditional FRPs, small molecules bonded to fiber surfaces are known to increase fiber-matrix interface strength and composite performance. The presence of a CNT sizing layer on the fiber surface presents a unique challenge for understanding the role of interface structure on durability in these hierarchical systems. In previous work, we found the CNT networks extend the lifetime of the FRP composites when exposed to water [1]. However, we were not able to identify direct evidence of alumina hydration by any physical or chemical characterization methods or visually observe changes in the interior fiber surfaces of the non-CNT FRP. Further, the kinetics of the aluminaborosilicate hydration reaction was largely unknown for this commercial material. As interfacial bond degradation has a significant impact on composite strength [2], this follow-on work examines in detail the alumina fiber hydration mechanism without the matrix polymer.

Experimental

In this work, two fiber systems, plain alumina oxide fibers (control) and alumina fibers exposed to the CVD growth process without reactants to generate CNT growth (CVD fibers), are immersed in deionized water at 60 °C up to 15 days. The fibers were removed from the water at different exposure times and the extent of hydration was quantified using Fourier transfer infrared – attenuated total reflectance

spectroscopy (FTIR-ATR), scanning electron microscopy (SEM), and thermogravimetric analysis (TGA).

Results and Discussion

The hydration of the alumina fibers proceeds at a rapid rate, affecting the surface of the Al₂O₃ in as little as 24 hours. The control fiber surfaces convert to platelet-like structures identified as pseudo-boehmite (and boehmite at long exposure times), in this aggressive environment [3]. FTIR-ATR measurements show the presences of boehmite on the fibers in as little as 1 day.

TGA was used to track the amount of bound water on the exposed fibers. The exposed fibers were ramped 10 °C/min to 1000 °C and held for 15 minutes to quantify the weight loss. Dehydration of bound water occurs over a broad range from 120 °C to 800 °C and the average mass loss over this temperature range was used to track the degree of hydration. It is noted that these conditions were not enough to fully dehydrate the sample to the original pre-exposure state. Therefore, the mass loss measured in TGA is likely due to bound water that is not fully incorporated into the hydrated crystal. The average mass loss increased non-monotonically with exposure time. At 24 hours (1 day), the water loss was 5 % by mass and reached an asymptote near 12 % by mass at 15 days.

SEM imaging was used to monitor the surface of alumina fibers for visual changes. In 1 day the presence of pseudo-boehmite crystals were evident on the surface of the bare fibers. The reaction proceeds from the exterior to the internal fiber surface. Figure 1 shows an example of a control alumina fiber after a 15 day exposure at 60 °C. This boehmite structure is brittle and weak. There were many images where the cracked boehmite exposed unreacted alumina beneath. We find that the CVD process alters the water absorption of the alumina fibers. The result is the conversion of the alumina along a parallel path to Bayerite. We will describe how the CVD process alters the fiber surface that mitigates the alumina hydration process.

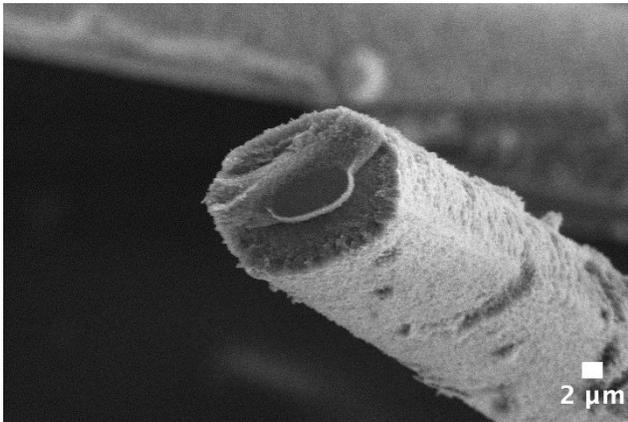


Figure 1: Fiber surface after HT-15 (60 °C, 15 days)

Conclusions

The bare aluminoborosilicate fibers hydrate quickly with direct water contact. The reaction products, pseudo-boehmite and boehmite, were readily observed using FTIR-ATR, TGA, and SEM imaging. These products were not found on the internal fiber surfaces of the FRP composite. This confirms that the strength reductions in the Al_2O_3 composites observed in the previous study was caused by the loss of fiber-polymer interfacial debonding, where water molecules diffuse to the composite interfaces and sufficiently separate the adjoining fiber and polymer surfaces, leading to poor load transferability between the structural components.

References

1. Krishnamurthy A., Hunston D.L., Forster A.L., Natarajan B., Liotta A.H., Wicks S.S., Stutzman P.E., Wardle B.L., Liddle J.A., Forster A.M. *Carbon*, 2017, 125, pp 63-75.
2. Gaur U, Miller B. *Polymer* 1990, 11, pp 217–22.
3. Wefers K, Misra C. *Oxides and Hydroxides of Aluminum*. Alcoa Tech Pap 1987, 19, p 100