Lessons for New Classes of Inorganic/Organic Composites from the Spicules and Skeleton of the Sea Sponge *Euplectella aspergillum*

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ABSTRACT

Studies have been carried out on the structures and mechanical characteristics of an unusual family of sea sponges under the classification of *Hexactinellida,* genus *Euplectella.* The sponge spicules have been of interest to materials scientists because of their potentially important optical, coupled with mechanical, properties. The structures of the class *Hexactinellida* are characterized by a concentric ring appearance in the cross-section, which is a composite of hydrated silica, coupled with silicatein as a thin layer at the ring interfaces. The mechanical behavior and the toughness of the spicules have been examined with the aid of a special fiber testing method, coupled with scanning electrom microscopy (SEM) observations. It appears that there may be common mechanisms underlying toughness in rigid natural composites with high ratios of mineral/organic phase. In addition, novel pressurization tests of a portion of the sponge skeleton have provided information about the resilience of the skeleton, which resembles a self-supporting glass winding of a cylindrical composite structure.

INTRODUCTION

In recent years, the design of new classes of hybrid ceramic/organic composite materials has been strongly influenced by biomimetic considerations. For example, shell structures composed of >95 v/o ceramic phase, with a minor component surrounding the ceramic components, have shown very high levels of toughness when compared with monolithic ceramics of the same material. In a similar vein, sponge spicules, comprising a predominantly glass phase (hydrated silica) and thin layers of a silicon protein (silicatein) have demonstrated much higher toughness than monolithic silica [1,2].

By way of sponge classification, in general, sponges with rigid skeletons that live in warmer waters are primarily mineralized from calcium (calcareous), and those sponges with rigid skeletons that inhabit cold, or deeper, waters are mineralized from silicon. This observation also conveys to the thin organic layers that exist in shells and spicules, as they are calcium-based proteins, or silicon-based proteins. Figure 1 shows a classification system for sponges (figure developed from data in Bergquist, [3]), and indicates the genus of the sponge of interest in this study, *Euplectella aspergillum* (also known as the Venus Flower Basket), which falls under the class *Hexactinellida*.

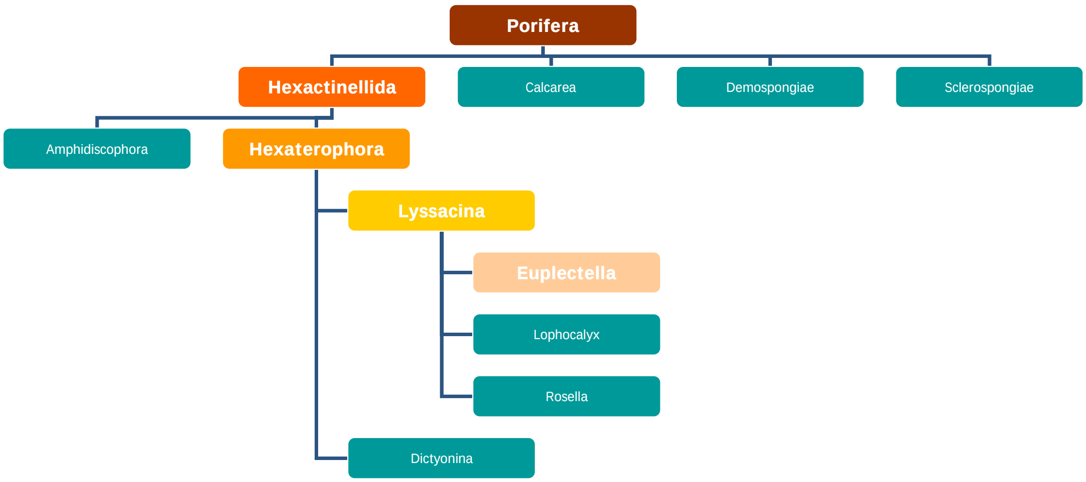

Figure 1. Sponge classification (derived from Bergquist [3]).

Much has been written in recent years about silicon biomineralization, and excellent summaries of the biology of the relevant processes are available from the work of Morse *et al.* [4-6]. There has been considerable interest in the optical characteristics of *Euplectella aspergillum*, as indicated in the papers of Aizenberg *et al.* [7-9]. The present work has to do with the mechanical behavior and mechanisms that control those properties in sponge spicules, and summarizes our work during the past year on the structure/mechanical property relations in the unusual construction of the skeleton of this sponge, which is shown in Figure 2, below. The dimensions of the skeletons vary somewhat; the specimen shown is ~300mm in length and tapered, from ~ 35mm at the top to ~20mm near the bottom end, where the cylindrical structural form begins. The outer upper-half portion is also ringed by two continuous ribbed collars, extending at about 45 degree angles; some specimens have a pronounced curvature, from bottom to top; the inner surfaces have no protuberances, and are smooth.

In terms of functionality, the skeleton assists in maintaining a rigid, open structure for the easy passage of nutrients. However, the narrower end, which is anchored in the ocean floor, is also subject to bending, and perhaps small torsional stresses in the ocean currents. The cylindrical structure of the skeleton is very similar (without the protruding ribs) to the weave of

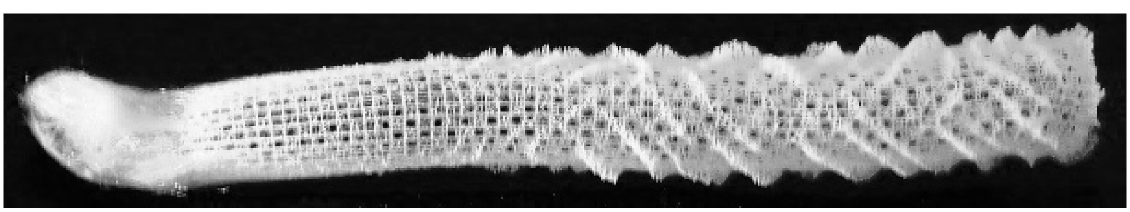

Figure 2. Skeleton of *Euplectella aspergillum* (approx. 1/2 actual size).

glass fibers in typical cylindrical glass-reinforced polymer-based composites. Such cylinders are designed for rigidity as well as resistance to complex stress states. This interesting similarity led to our study of the skeleton, as well as of the individual spicules that make up the structure.

The earliest observation of the remarkable toughness of similar sponge spicules was noted in the work of Levi *et al.* [1], which also showed the concentric ring structure of the spicule of the sponge *Monorhaphis* (another sponge of the *Hexactinellid* class). The structure of its spicule is shown in Figure 3. Levi *et al.* [1] reported unusually high toughness values of the spicules that were tested in bending (in comparison with that of silica glass), and they associated this with the concentric ring structures of the spicules. These results were also confirmed by Sarikaya *et al*. [2] in a different *Hexactinellid* sponge, *Rosella racovitzea*.

The purposes of this work were to study the mechanical behavior of the sponge spicules in *Euplectella aspergillum*, otherwise known as the Venus Flower Basket (and identified in the subsequent text as *EA*), in particular, to shed light on the microstructural mechanisms that underlie toughening in this very interesting glass/organic composite material, and also, to try to understand the structure and properties of *EA.*

On a comparative basis, the diameters of the *Hexacinellida* fibers in the reported works varied from about 40μm [7] to as much as 8000μm (Chun, as cited in [1]).

EXPERIMENTAL DETAILS

Because of the small diameters of the individual fiber spicules of the *Euplectella* specimens, it was initially thought impractical to plan bending tests, as had been done in the prior studies [1,2]. Thus, for the determination of strength, stiffness, and toughness, we relied on the new tensile testing method for fine fibers that was developed at the Oak Ridge National Laboratory, and which resulted in a new ASTM standard for fiber testing [10]. This testing method was developed for individual fibers of ceramics glasses, carbon, and other advanced fibers, where gripping, alignment, and other difficulties are encountered with conventional testing methods. In addition, the earlier experiments dealt with bending loads, which are tensile

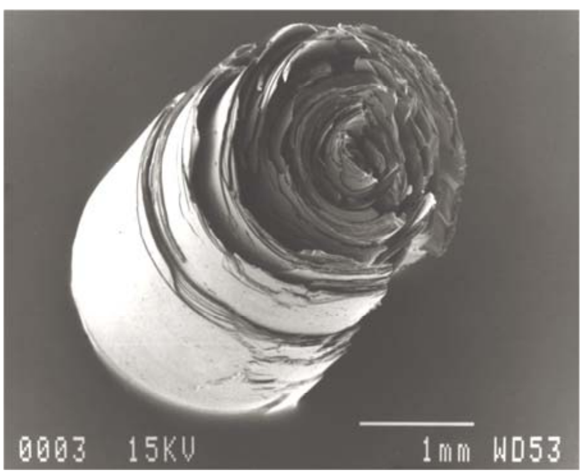

Figure 3. Scanning electron micrograph of the *Monorhaphis* sponge spicule fracture (courtesy of P. LeHeude).

on one side of the beam specimen, and compressive on the other side, and may not be as informative as a tensile test. Finally, the fine fibers of interest in *EA* would have been difficult to test in a bending configuration.

The specimens of *EA* were obtained from commercial shell collecting sources, and there was no certainty about their prior treatment. However, all external surficial organic matter had been removed.

The individual fibers which were tested were taken from the root end of the *EA*, the section which sits anchored in the ocean floor. Those fibers were typically the longest and straightest, in the entire skeleton. The diameters of the long fibers in the base of the skeleton ranged from about 25µm to 50µm. These were compared with the mechanical behavior of e-glass fibers of 15µm to 35µm in diameter.

The fibers were carefully cut with sharp clippers, and handled with care to prevent accidental damage. Mounting tabs were prepared from a template, and copied onto manila folder material, to provide some rigidity and support to the glass fibers and the spicule fibers during mounting in the testing machine. Both sets of fibers were individually mounted by means of an epoxy adhesive (Shell Epon®828). The distance between the epoxy adhesive drops (about 25 mm) defined the gage length. The mounted specimens were allowed to dry for 24 hours. The tabs were then mounted on the testing machine, and the central supports around the fiber to be tested were carefully cut. The procedure is comprehensively described in reference [10].

Tensile tests were conducted in the ORNL High Temperature Materials Laboratory on an electromechanical testing machine. The fibers were tested at one of two speeds, 5µm/s or 20 µm/s, to study the viscoelastic component to the tensile properties that might be conveyed by the thin silicatein layers between the hydrated silica rings.

RESULTS AND DISCUSSION

<u>Tensile test results</u>

The tensile tests conducted at ORNL showed that the toughness of the spicules did not differ markedly from that of the e-glass fibers tested, although the curves had different shapes. In those cases where slippage occurred in the tab-mounted specimens, the data were discarded. A representative load-extension curve of a spicule test is shown in Figure 4. Unlike the tensile load-displacement curves associated with the tensile evaluation of silica fibers, which were linear up to failure, the tensile load-displacement curves of *EA* fibers exhibited non-linear behavior. Figure 4 depicts the load versus cross-head displacement curve obtained from the tensile evaluation of an *EA* fiber. We have interpreted the mechanical behavior as follows: The curve exhibits a linear regime (A-B), which corresponds to the elastic response of the fiber. At point B, the outer layers of the *EA* fiber crack, leading to a change in the slope of the curve. Segment B-C in the load versus displacement curve corresponds to the response of the cracked structure. At point C, a major cracking event occurs, resulting in a significant increase in the compliance of the material and in the fracture of the innermost cylinder of the *EA* fiber. Because cracking of the concentric outer cylinders is accompanied by deflection of those cracks at the viscoelastic organic interphase that exists between the cylinders, cracking occurs at different planes along the length of the *EA* fiber. These processes lead to our proposed model of the formation of a telescopic structure as depicted in Figures 5 and 6.

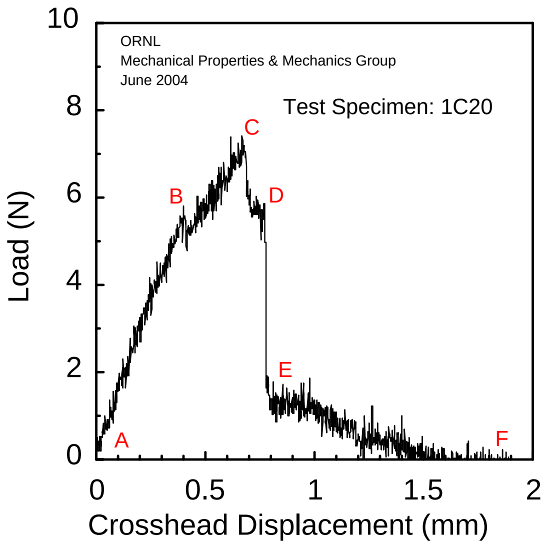

Figure 4. Load-displacement curve of a typical *EA* fiber.

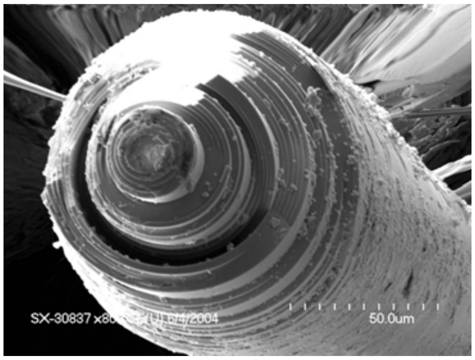

Figure 5. Scanning electron micrograph of tested *EA* fiber illustrating the telescopic structure that develops.

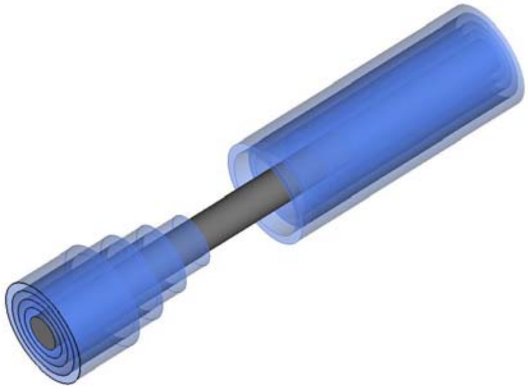

Figure 6. Schematic (model) of damage progression in *EA* fiber during tensile loading; cracks formed in the outer concentric cylinders are deflected at the organic interfaces between the cylinders, leading to the development of a telescopic structure.

The various crack divergences, and the energy dissipated at the viscoelastic thin layers between the hydrated silica rings, are considered to be part of the toughening mechanism of the spicules.

Loading rate effect

The two loading rates used to test the spicules were not remarkably different, 5μ/s and 20μ/s. The effect of changing the loading rate modestly was quite noticeable, as shown in Fig. 7. The higher loading rate resulted in markedly higher fracture stresses, but lower strains to failure.

Observations on fracture

An examination of the fracture surfaces of the spicule fibers that were pulled to failure shows one of the problems for analysis of the comparative toughness of spicule vs. e-glass. It is known that very little reduction in area occurs during the extension of e-glass fibers before they fail. Thus, the use of initial area to calculate the fracture stress of that material is warranted. This is clearly not the case for the spicule fibers. Because we can associate the central region of Figure 8 with fast fracture (the region of the load-displacement plot between D and E in Figure 4), we can, with some surety, assume that the central region carried the load on the spicule at the point just preceding the major load drop. Thus, we can calculate a true stress from this information. Since the load-bearing diameters of the spicules were not measured during the tests, none of the prior true stresses (following the fracture of the first outer ring) could be calculated. Nonetheless, the relative toughnesses of spicule and silica glass in tension were not as

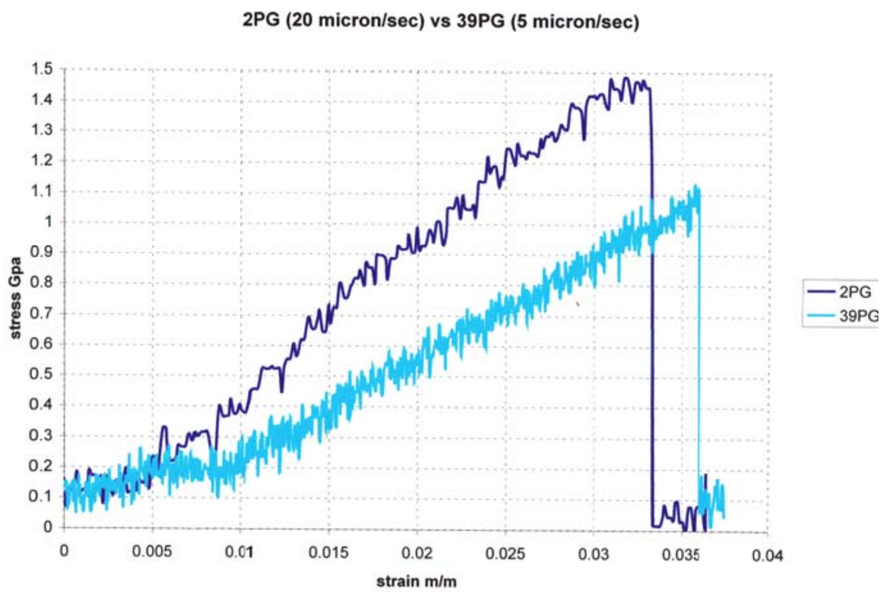

Figure 7. Effect of loading rate on the mechanical response of *EA* spicule fibers.

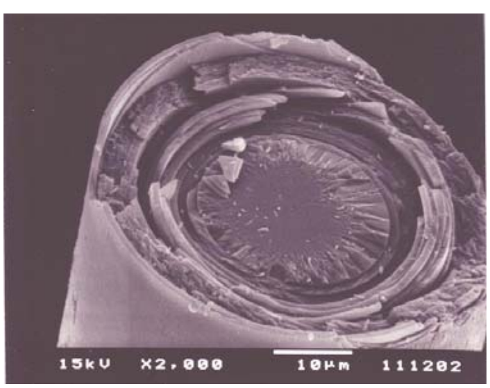

Figure 8. Fracture surface of spicule fiber tested in tension, showing central region with evidence of fast fracture (SEM).

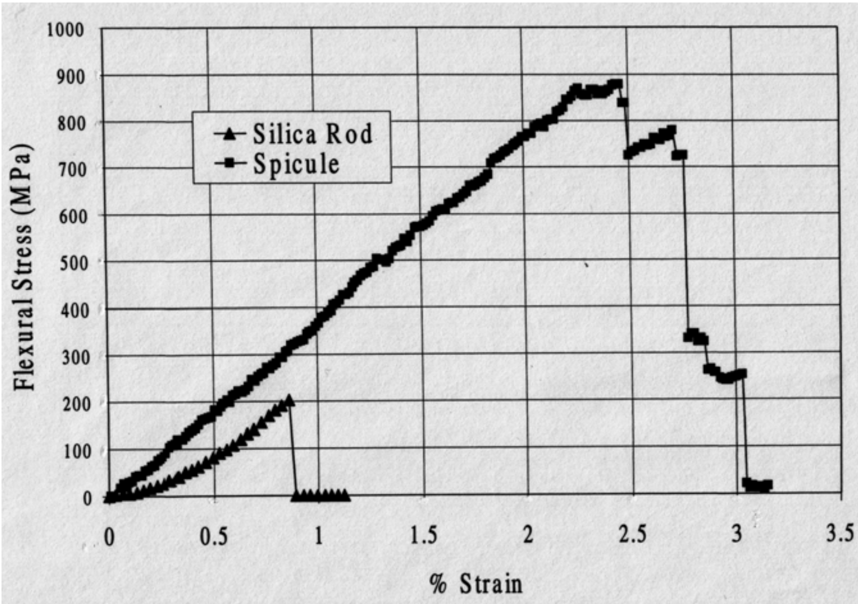

Figure 9. Bend test results on a spicule fiber vs. silica rod (from Ref. 2).

dramatically different as in the case of the bend tests done in Reference 2 (on another genus of *Hexactinellid* sponge), and indicated in Figure 9.

Another important effect on toughness was indicated in SEM images that showed cracks which initiated in the hydrated glass cylinders were stopped at the very thin protein interfaces.

CONCLUSIONS

The results of the tensile tests of the spicules in comparison with e-glass were at first surprising, since the prior studies, which had been done in bending [I,2], showed much greater toughness in the spicules. However, the bend test involves much larger shear stresses, in comparison with shear in the tensile test, and we propose that the many viscoelastic layers between the concentric glass cylinders have a more substantial effect during bending. Further study of the comparison between bending and tension tests on *EA* fiber spicules will be attempted with the help of a DMA apparatus, operating in a static mode for bending of fine fibers and spicules, as well as utilizing AFM methods. In terms of the functional loading condition, it seems that the *EA* sponge would be subjected primarily to bending, rather than tensile, loads while anchored in the sea-bed. Thus, the structure of concentric rings of hydrated silica, separated by viscoelastic silicatein, would be quite tough in that environment, as compared to monolithic silica, indicating that nature has constructed *EA* wisely!

This study concludes that the effects of very thin layers of a resilient viscoelastic phase at the boundaries of a normally brittle constituent appear to have very large effects on toughness of natural composites, as had been proposed earlier [11].

ACKNOWLEDGEMENTS

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REFERENCES

1. C. Levi, J.L. Barton, C. Guilemet, E. Le-Bras, and P. Lehuede, *J. Mater. Sci. Lett.* **8,** 337 (1989).
2. M. Sarikaya, H. Fong, N. Sunderland, B.D. Flinn, G. Mayer, A. Mescher, and E. Gaino, *J. Mater. Res.* **16**, 1420 (2001).
3. P.R. Bergquist, **Sponges**, University of California Press, Berkeley, 13 (1978).
4. K. Shimizu, J. Cha, G.D. Stucky, and D.E. Morse, *Proc. Natl. Acad. Sci.* **95**, 6234 (1998).
5. J.C. Weaver, L.I. Pietrasanta, N. Hedin, B.F. Chmelka, P.K. Hansma, and D.E. Morse, *J. Struc. Biol.* **144**, 271 (2003).
6. J.L. Sumerel and D.E. Morse, in *Silicon Biomineralization* (Springer-Verlag, New York) 225 (2003).
7. J. Aizenberg, A. Tkachenko, S. Weiner, L. Addadi, and G. Hendler, *Nature* **412,** 819 (2001).
8. V.C. Sundar, J. Grazul, and J. Aizenberg, *Mat. Res. Soc. Symp. Proc*. **224,** 115 (2003).
9. J. Aizenberg, V.C. Sundar, A.D. Yablon, J.C. Weaver, and G. Chen, *Proc. Natl. Acad. Sci.* **101**, 3358 (2004).
10. American Society for Testing and Materials, *ASTM C1557-03, Standard Test Method for Tensile Strength and Young's Modulus of Fibers*, ASTM, West Conshohocken, PA. (2003).
11. G. Mayer, *Cer. Bull.* **83,** 9301(2004).