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Acta Biomaterialia 3 (2007) 377–382
Acta BIOMATERIALIA
www.elsevier.com/locate/actabiomat

Effects of loading rate on the mechanical behavior of a natural rigid composite ☆

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Received 22 May 2006; received in revised form 10 August 2006; accepted 26 September 2006

Abstract

The effects of loading rate variations on the stress–strain behavior, failure mechanisms, fracture modes, and energy-dissipating capability of the spicules of the sponge *Euplectella aspergillum* have been investigated. Comparisons were made with similar measurements on a silicate glass. It was concluded that the very thin (5–10 nm) organic layers that are interspersed with thicker layers of hydrated silica in the concentric ring structure of the spicules strongly influence all aspects of the mechanical behavior.

Keywords: Sponge spicules; Mechanical behavior; Loading rates; Energy dissipation

1. Introduction

Interest in sponge spicules stems from their interesting combinations of stiffness, strength and energy-absorbing capabilities. Important lessons may be learned from the structure–property relations found in sponge spicules for the practical purpose of designing new synthetic composite materials. Earlier work has concentrated on the strength and stiffness of spicules, with only passing note of their flexibilities and damping capacities. The evidence for flexibility and viscoelasticity in organic and hybrid organic systems stems from observations described by Levi et al. [1], Sarikaya et al. [2], Mayer et al. [3], and from the bodies of evidence in scientific papers and in a comprehensive collected volume of papers [4–6]. In the first instance, observations were made of a long cylindrical spicule of a siliceous sponge comprising hydrated silica ($SiO_2 \cdot nH_2O$ where n is 2–5) sandwiched with thin layers of proteinaceous material (in a concentric ring structure form in cross section, as in Fig. 1). When the spicule was bent into a circular form, it did not fail, and, when the load was released, the original shape recovered, although nothing was stated about whether this happened instantaneously or over a period of time. Such behavior was observed in long, thin, cylindrical spicules of *Hexactinellid* sponges. Subsequent studies confirmed these observations. Experiments on spicules of a sponge that were performed at Oak Ridge National Laboratory, and cited in Ref. [3], included several tests that were carried out at different strain rates. Those results were not studied in any detail at the time, but there was enough information to indicate that a notable rate sensitivity existed in the spicule fibers of *Euplectella aspergillum* (Fig. 2).

The ability of the unusual composite structure of the spicule to dissipate energy during deformation, before catastrophic failure, is the major reason for interest by designers of composite structures. Energy dissipation is a very important factor that can be beneficially put to use in advanced synthetic composite materials.

It was decided to conduct a much more detailed investigation into the rate sensitivity of this hybrid composite material, with emphasis on the effects of loading rate and the thin organic layers on energy dissipation. The organic layers that exist in the spicules of the sponge that were studied are of the order of 5–10 nm in thickness, and it

☆ Research presented at the TMS 2006 Biological Materials Science Symposium.

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1742-7061/$ - see front matter
doi:10.1016/j.actbio.2006.09.008

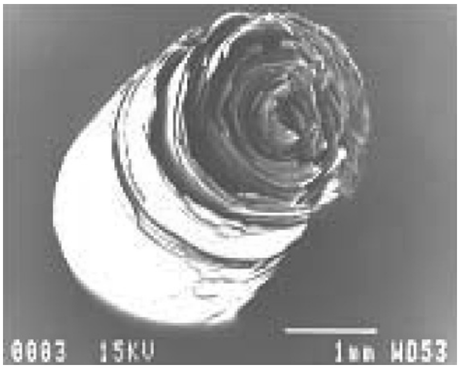

Fig. 1. Cross section of *Monorhaphis* spicule (Courtesy of P.Lehuede).

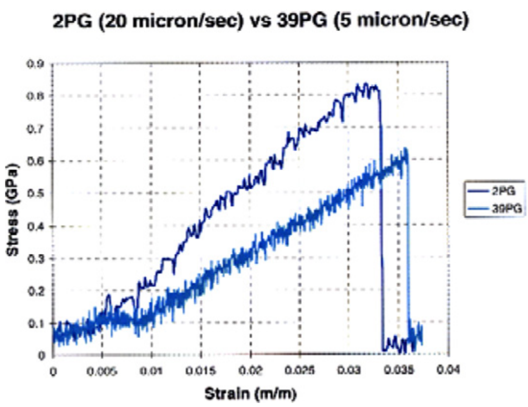

Fig. 2. Stress–strain curves for spicules under two different strain rates [3].

has not been possible to interrogate them directly using atomic force microscopy methods, as was done in the case of nacre by Smith et al. [7]. Tests at different loading rates were conducted in order to shed more light on the elastic and viscoelastic characteristics of the thin organic layers. Such layers have been identified in other, different, sponge species by Sumerel and Morse as several different silicateins [8], i.e. classes of silicon proteins. Although it was not within the scope of this study, the authors believe that, while the organic constituents of the thin layers of the sponge that was studied in this work are probably different from the silicateins that have been identified, they will still be proteins that are based on silica.

2. Materials and methods

E. aspergillum sponges were selected for this study, because earlier specimens of *Hexactinellids*, of which this system is a representative, had shown interesting combinations of resilience and time-dependent mechanical behavior, along with substantial strength and stiffness. Also, a number of the skeletons of this sponge were readily available to us for the research. On the other hand, handling, gripping and testing of the very fine fibers, on the order of 50 μm, was a challenging task. All mechanical testing was carried out on specimens from two sponge skeletons

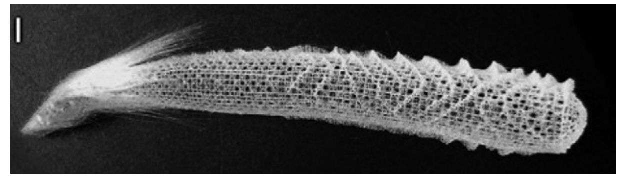

Fig. 3. Skeleton of *E. aspergillum*, showing spicule fibers that were tested (taken from the separate fibers toward the left, basal side.) Scale bar = 1 cm.

(Fig. 3 from an unpublished example), working with only smooth, straight sections of spicule fibers, from the approximate regions noted on Fig. 3. Fiber sections at the very basal end of the skeleton tend to have short branches, or an anchor-like end section [9]. The latter fiber sections were discarded from consideration for mechanical testing, since their stress states would have been too complex for analysis. The diameters of fibers included in the mechanical tests ranged from 40 μm to 70 μm. It should be noted that the cross section of the fibers is different from what is seen in Fig. 1, in that a larger inner core of hydrated silica is present, as shown schematically in Fig. 4. That inner core has been related to the optical transmission characteristics of *E. aspergillum* [9]. At the very center of the solid inner core is a small square cylindrical core (of probably a) protein.

As a basis for comparison, fibers of a silicate glass, identified as an electronic-grade glass, EMGO 360, and containing BaO and Na_2O in a silicate glass, with diameters 40–70 μm (that had been drawn from the melt by NIST) were included for testing and analysis. The sponge skeletons were generously donated by Nature's Creations® of Sammamish, WA. Those skeletons had been pre-treated with a diluted bleach solution and subsequently rinsed with distilled water to remove both the outer softer "spongy" layers and any debris that might have been present. Fiber diameters were carefully examined for flaws with optical microscopy and diameters were also measured for the smooth fibers that were selected for mechanical testing.

Tests at different loading rates were conducted in three-point bending, using a dynamic mechanical analysis (DMA) system (Perkin–Elmer Model 7e), in both the static and dynamic modes, in order to shed more light on the elastic and viscoelastic characteristics of the thin organic layers. Both the spicule fibers with the concentric ring structure and the silica fibers used as reference material were tested under similar conditions. Thirty samples of each type of fiber were tested at the high loading rate in order to establish a reasonable database. Ten samples of each fiber were tested at low and moderate loading rates. Loading rates of 1 mN/min, 10 mN/min, and 100 mN/min were employed. After fracture, the fiber segments were carefully collected for examination by scanning electron microscopy (SEM).

Frequency scans were also conducted on the spicules and glass fibers in order to examine damping characteristics. The tests scanned from 1 Hz to 51 Hz at a load of

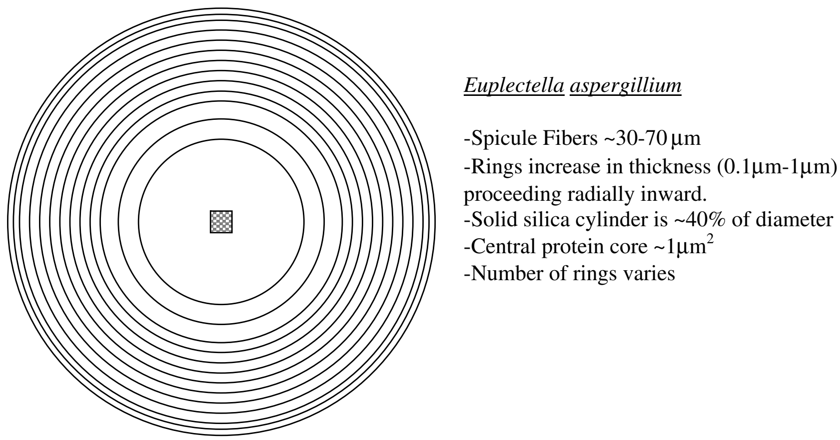

Fig. 4. Schematic drawing of *E. aspergillium* spicule. Note: drawing is not to scale.

10 mN. Ten samples of each fiber were tested under cyclic DMA conditions.

It was estimated that, over a three-month period of DMA testing, neither the room temperature (70 °F) nor the relative humidity (40%) changed more than 5%, and were thus considered to be constant.

3. Results and discussion

The findings of two sets of data are presented here, one that summarizes the loading rate effects, and the other that addresses the damping characteristics of the fibers. Both sets of data enable comparisons of the behavior of the spicule fibers with those of synthetic glass fibers of quite similar diameters.

3.1. Loading rate effects

The data for the mechanical properties of both the spicule fibers and of synthetic silica fibers are presented in Figs. 5–7. The data from the DMA tests in the static mode (so-called even though the loads were dynamically, but not cyclically, applied) show that for glass there is only a small change in strength with changing loading rate. However, data for the spicule show that the two higher loading rates result in a much higher true stress than the lowest loading

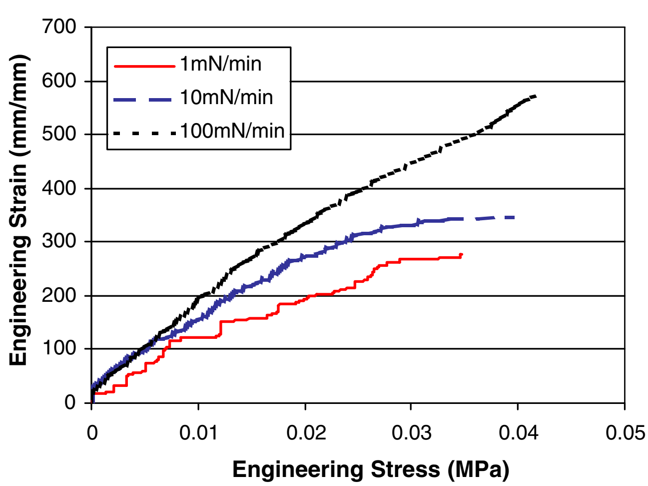

Fig. 5. Spicule: engineering stress–strain at three loading rates.

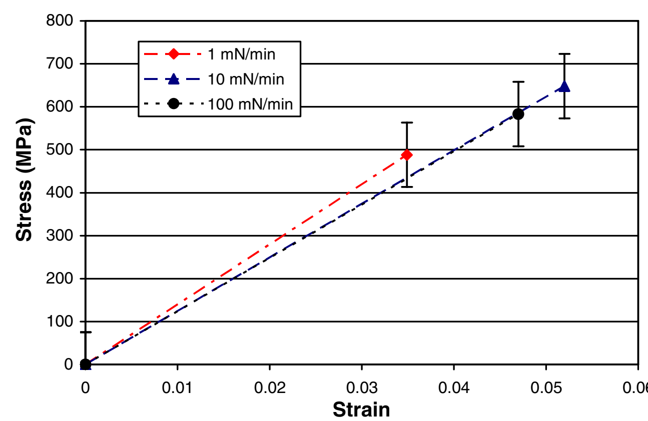

Fig. 6. Glass: true stress vs. true strain at three loading rates.

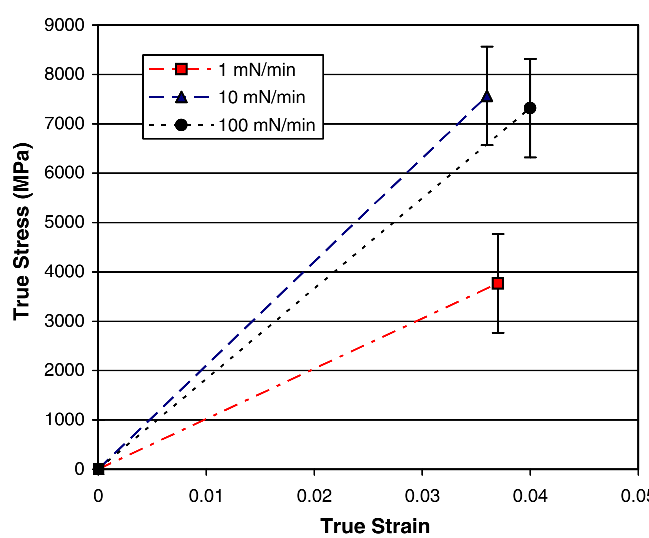

Fig. 7. Spicule: true stress vs. true strain at three loading rates.

rate. The difference in fracture stress between the two higher loading rates is very small and was deemed to be insignificant. However, the maximum strain for the highest loading rate is larger than that for the moderate loading rate.

Energy dissipation values can be derived from either the engineering stress–strain curves or the true stress–true strain curves that are calculated from final fracture area and engineering stress–strain. Those values from the engineering stress–strain curves serve as a lower bound of the energy absorption of the spicules, and the actual value is closer to that derived from the true stress–strain curves, since the cross-sectional area of the spicules changes dramatically throughout the duration of the test, and a much greater volume of the spicule contributes to energy dissipation through mechanisms such as crack diversion, crack bridging and other means. This is shown in the fracture images of the spicules and also in the load–displacement curves (Fig. 5). In the load–displacement curves, the changing slope probably indicates deformation and/or fracture events in the spicule, such as those described above.

Table 1 shows that the energy dissipation for glass does not change appreciably with changing loading rate. For the spicules, the energy dissipation increases with increasing loading rate. The spicule and glass fracture surfaces are shown in Fig. 8. In the case of the spicules that were tested at the two lower loading rates, fracture took place in packets, where several layers of hydrated silica break at the same time. The fracture surfaces for the lowest loading rate shows that the packets are quite large, and the fractures are quite complex. At the highest loading rate, it appears that individual rings of hydrated silica appear to fracture independently of one another. This may be related to the increased toughness values, if more energy is expended in individual ring fractures. But, undoubtedly, other energy-dissipating phenomena are also involved. Confirmation of a continuing softening trend in the spicules at higher loading rates has been confirmed by several tests done at 200 mN/min (though these are not included in the plotted data).

In fact, the highest rates that were used in these tests would probably not be encountered in the natural environments of the *E. aspergillum* sponge. Nonetheless, it was interesting to observe a reversal of the load extension data at the highest rate for the spicule fibers. It would not be unreasonable to expect that behavior could be caused by adiabatic heating in the organic layer. Such behavior might be expected since stress-softening may be expected to occur

Table 1
Energy dissipation values for glass and spicules at varying loading rates

Loading rate (mN/min)	Energy dissipation (MPa)		
	Glass	Spicule upper bound	Spicule lower bound
1	8.1 ± 3.5	69.1 ± 34.9	5.4 ± 1.8
10	16.7 ± 8.3	132.2 ± 47.4	6.6 ± 1.9
100	14.1 ± 7.3	166.6 ± 66.1	11.0 ± 3.9

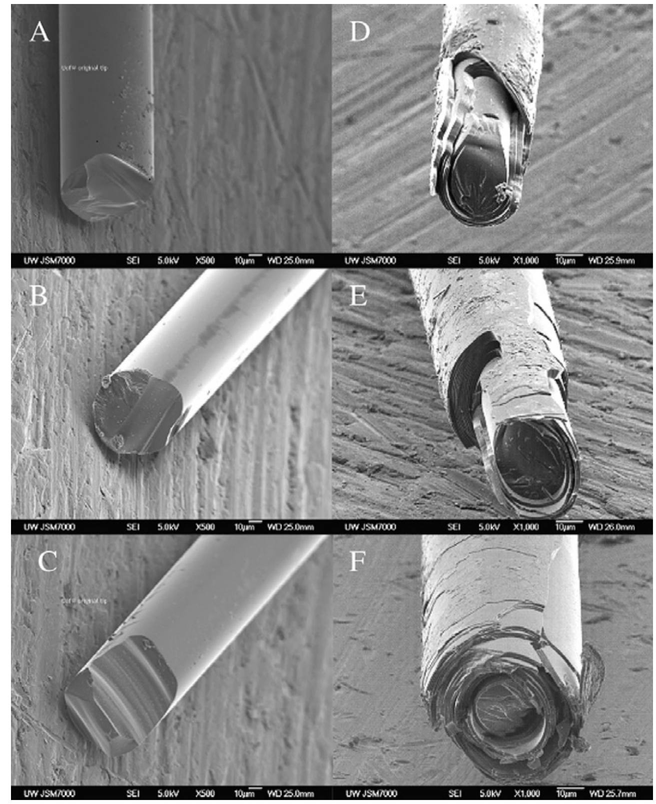

Fig. 8. Fracture surfaces of (a) glass at 1 mN/min, (b) glass at 10 mN/min, (c) glass at 100 mN/min, (d) spicule at 1 mN/min, (e) spicule at 10 mN/min, and (f) spicule at 100 mN/min.

in proteins, in a manner not unlike that reported by Waite et al. [10] on byssal threads of mussel collagen. That behavior would also be favored by the poor thermal conductivity of the hydrated glass in the adjoining layers.

3.2. DMA testing in the dynamic mode

Dynamic scans over a range of frequency are shown in Figs. 9 and 10. E' is Young's storage modulus, and is a measure of the energy stored elastically. E'', the loss modulus, is a measure of the energy lost as heat, and the loss tangent, or $\tan\delta$, often termed as damping, indicates how

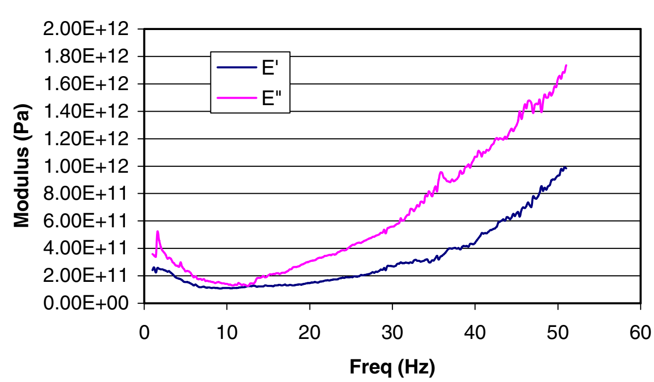

Fig. 9. Spicule: E' and E'' vs. frequency.

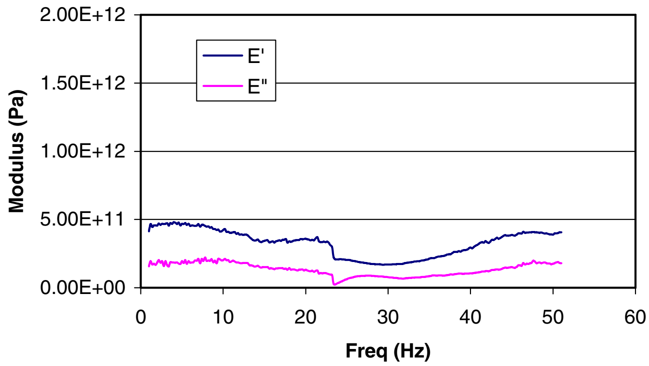

Fig. 10. Glass E' and E'' vs. frequency.

effectively a material loses or dissipates energy due to internal friction and to molecular rearrangements [14]

$\tan\delta = E''/E'$.

This is a very complex issue mechanically, in that the spicule fiber is a series of concentric cylinders of hydrated silica interspersed with very thin cylindrical rings of a complex protein adhesive, at differing distances from the central axis of the fiber. This complex system is vibrating in a bending mode, and, as it vibrates, the thin layers probably have overlapping influence on the damping processes that are taking place. The thin layers, of thickness 5–10 nm [11], have not been characterized as yet, but they appear to attach quite tenaciously to the silica surfaces [12]. They have also contributed to the energy-dissipating ability of the spicule fiber composite, which has been measured previously to be about six times greater than that of silica fibers, in either tension or bending [13].

Over the range of testing frequencies, E'' dominates for the spicule. However, in the synthetic glass, E', the elastic modulus, dominates, and no evidence could be discerned for losses.

Fig. 11 shows the $\tan\delta$ data for glass fibers and spicules. The glass fibers had no peaks on the $\tan\delta$ curve because there was no frequency, over the range examined, at which damping occurred. The $\tan\delta$ curve for the spicule had three peaks, each at a different range of frequencies. It is proposed that those are evidences of the controlling influence of the thin organic layers on damping at several different frequencies. The peaks are thought to be broad due to a number of layers that damp at varying frequencies. These curves are now being studied to try to determine more specifically the reasons for the shapes, positions of minima and maxima, etc.

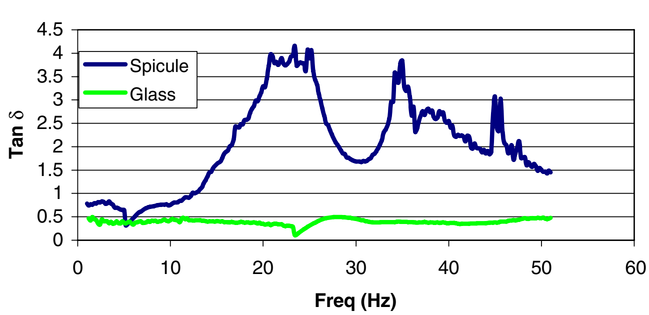

Fig. 11. $\tan\delta$ vs. frequency for glass and spicule.

3.3. Mechanisms of importance for continuing study

It is also noted that, mechanistically, the thin layers, if proteins, may deform by unfolding processes due to the layers shearing. At this time, no analysis has been done, to our knowledge, of restraints to unfolding processes in proteins that are arrayed in thin, constrained (by adjoining silica on both sides) layers of the order of 5–10 nm. In addition, the mode of anchoring of the organic constituent to the silica at their interfaces is presently unknown, and assumptions about delamination at the interface between constituents vs. stretching and breaking of molecular bonds have not been made, nor calculations attempted.

4. Conclusions

It has been demonstrated that a small volume of organic material incorporated in very thin annular concentric rings of a hydrated silica/organic composite fiber spicule has a very strong effect on energy dissipation (a measure of toughening), as well as on the damping characteristics of the composite. Because of the architecture of the layered structure, structural damping takes place over a broad range of frequency, no doubt due to overlapping effects of the thin organic layers at different distances from the central core. In contrast, no such rate effects were observed in the glass fibers

The molecular mechanisms that are responsible for the interesting and potentially important mechanical behavior have yet to be identified. These unknowns have to do with the deformation mechanisms and characteristics of very thin (5–10 nm) films of organic materials that are constrained between rigid interfaces, and the interfacial bonding that may play a key role in energy dissipation.

The energy dissipation of the spicule fibers substantially exceeded that of glass fibers at all three decades of loading rates that were examined. However, the modes of fracture of each class of fiber appeared to be distinctly different. This may be due to the differences in the apportioning of energy into the various modes of energy dissipation, i.e. creation of new surfaces, crack bridging, delamination, heating, changes to the structural arrangement of the organic adhesive and other possible mechanisms. It is proposed that adiabatic heating may be responsible for some of the energy loss at the highest loading rates for the spicule fibers.

Acknowledgements

The authors thank Paul Kannikeberg for assistance with the mechanical tests, and Dr. Tom Murray, for timely help with scanning electron microscopy. The authors also express their appreciation to Oak Ridge National Laboratory for use of their equipment in the early stages of tensile testing of the fibers, and to Patrick Curry of Nature's Creations for the donation of the specimens that were used in this study.

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