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Influence of moisture on the mechanical behavior of a natural composite

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ABSTRACT

The effects of moisture on the mechanical properties of the spicules of the sponge *Euplectella aspergillum* have been investigated. Determinations were made with the aid of a dynamic mechanical analyzer in both the static and dynamic modes, as well as imaging of the failed surfaces with scanning electron microscopy. For comparison purposes, melt-grown glass fibers of similar diameters were also studied in both distilled water and seawater. That exposure reduced both the stiffness and strength of the spicules. In addition, the energy required to achieve complete failure decreased in moist environments. The data for the wet spicules in both aqueous media showed decreasing values of energy dissipated until catastrophic failure compared to dry samples. The strength of wet glass decreased when compared with the dry condition, and the elastic modulus was also reduced. The most marked influence of moisture was seen in the damping effects in moist spicule samples that were nearly an order of magnitude larger than the damping of dry spicules. This effect was attributed mainly to plasticization of the thin organic layers.

1. Introduction

Moisture is known to have a substantial influence on the mechanical behavior of natural materials as well as of synthetic materials, including glass [1]. The role of moisture in the viscoelastictity of biomaterials was reviewed broadly by Dorrington [2]. Work has been done on the effects of moisture on a variety of natural materials, ranging from spider silk [3] to the effects of moisture on insect cuticle and pine-cone bract by Vincent [4]. The mechanical properties of other rigid biological composite materials have also been shown to have substantially different values in wet than in dry conditions. For the case of mollusk shells [5], results generally showed lower strength and stiffness, but higher toughness. Such effects have been related to plasticization of the organic phases of the composite systems that were investigated.

Since siliceous sponges exist in seawater as well as in freshwater environments, they are always immersed in water, often cold and deep. Because of this fact, and in view of the observed effects of moisture on other rigid biological composites, it was considered essential to study such effects on the silica/organic composites that comprise sponge spicules and skeletons.

The spicules of the sea sponge *Euplectella aspergillum* consist of a layered structure of alternating concentric cylinders of hydrated silica, $SiO_2 \cdot nH_2O$, and thin organic constituents, probably proteins, in addition to an inner cylindrical hydrated silica core (a schematic diagram is shown in Fig. 1). Due to this unique structure, the spicules of this sponge have been shown to possess attractive combinations of mechanical properties, including strength, stiffness, resilience and energy dissipation, that exceed those of similar man-made materials, such as monolithic silica [6,7]. The spicules of a number of hexactinellid sponges have structures with interesting and potentially important optical and mechanical properties [8–10], although in deep ocean environments, where many of these sponges live, the ability to harvest energy from sunlight may be doubtful. However, nature has found ways to utilize the strength and stiffness of glass, and the flexibility and resilience of the thin organic interlayers of the spicules. These characteristics confer on the structure of the composite fiber an ability to dissipate large amounts of energy on both the static and dynamic levels [11,12].

The sponge *E. aspergillum* is usually found at ocean depths from 36 to 5050 m [13]. The skeletons of siliceous sponges are formed through biomineralization at cold temperatures (rather than at the high temperatures, on the order of 1500 °C, that are normally required to melt and form synthetic glass fibers). As the spicule fibers form the lattice-like skeleton, they either are fused together or are connected by a glue, to form the complex structure seen in Fig. 2.

Spicule fibers of mature sponges of *E. aspergillum* generally range from ~30 to ~70 μm in diameter and contain a central cylindrical structure that typically represents ~1/3 of the total diameter of the fiber, as shown in Fig. 1. In the center of this hydrated silica core is an axial filament of square cross-section that is about 1 μm on each side (probably proteinaceous, based on work on another hexactinellid sponge by Müller et al. [14]. Moving radially outward

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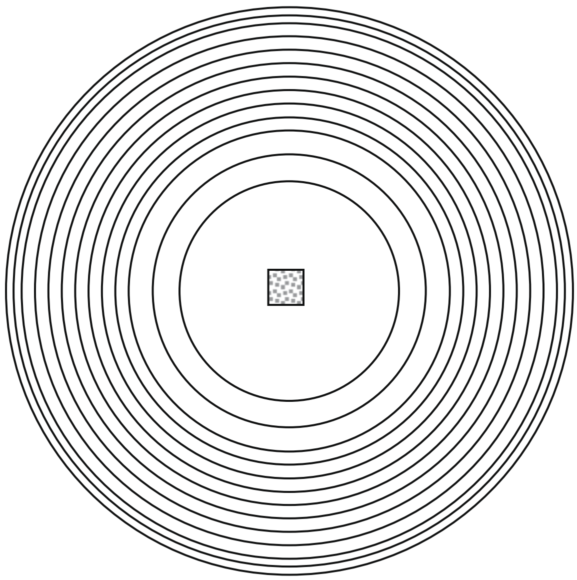

Fig. 1. Cross-section of *E. aspergillum* spicule fiber: the cylindrical fibers are ~30–70 μm in diameter; rings generally increase in thickness (0.1–1.0 μm progressing from outer to inner rings; solid silica cylinder is ~1/3 of the diameter; axial cylinder with ~1 μm square core of protein constituents; number of rings varies (typically 15–30); thin protein rings between hydrated silica glass cylinders of the order of 5–10 nm.

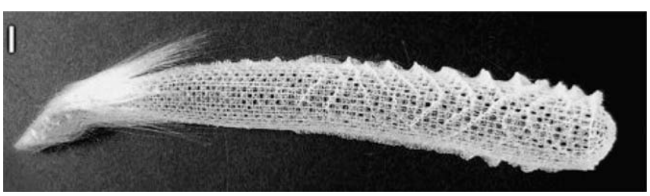

Fig. 2. Scale bar: 1 cm. *E. aspergillum* skeleton; length usually ranges from 6 to 32 cm and diameters from 1.5 to 5 cm.

Fig. 3. Skeleton of *Euplectella* sponge, indicating position of smooth fibers used in mechanical tests. ([9]; copyright 2004, National Academy of Sciences, USA) used with permission.

from the central core is a series of concentric layers alternating between a hydrated silica, $SiO_2 \cdot nH_2O$, and a very thin (of the order of 5–10 nm) protein phase. The protein phase makes up only about 2–3 vol.% of the spicule.

Organic phases have been found to play important roles in altering and controlling the mechanical behavior of moist biological composites, as noted earlier. Generally, the effects have been to lower the strength and stiffness, but with an observable increase in toughness. The major influence is believed to stem from plasticization of the organic constituent(s) of the composites [4].

Previous experiments have shown that, in bending as well as in tension, the capacity to dissipate mechanical energy in the sponge spicules was considerably higher than that shown by monolithic silicate glass [11]. Energy dissipation, in this case, is defined as the amount of energy that is expended up to the starting point of catastrophic failure. Walter et al. [12] found that a number of factors contributed to such increases in these fibers in the dry state. The primary focus of this phase of study was to define the extent that moisture affected the mechanical behavior of the complex composite that is the spicule, and perhaps, by extension, similar natural composites.

2. Materials and methods

2.1. General background

This study focussed on the mechanical response of both dry and wet spicule fibers of *E. aspergillum* in comparison with a baseline of fibers of melt-drawn glass fibers in dry and wet states under both static and dynamic conditions. The skeletons of the sponges from which the spicules were obtained had been donated by Natures' Creations of Sammamish, WA, and originated from a private collecting source in the Philippine Islands. There was no prior knowledge of handling, other than that the skeletons had been cleaned in a diluted bleach solution. The outer soft biological tissues had been removed from the skeletons. The spicule fibers were (originally observed as smooth) straight sections taken from near the base of the skeleton shown in Fig. 3. They ranged in diameter from about 30 to 70 μm. Although a baseline of opal (hydrated silica) would have been preferred for comparison, the scatter in the structures and properties of opal, combined with the fact that opal does not exist as a fiber, prevented such a choice. Thus, the glass fibers used as the base of comparison had been pulled from the melt through dies by NIST from an EMGO 360 lead-free electronic glass (comprising primarily SiO_2, but also small levels of Na_2O and BaO). The diameters of those melt-processed fibers ranged from 50 to 90 μm.

Each of the spicule fibers for analysis was taken from the same sponge in an attempt to avoid variations between different specimens of the same species. For example, it had been determined earlier [15] that the numbers of concentric rings in a spicule fiber could vary from about 15 to 30 or more in different specimens of *E. aspergillum* that were examined, and that those differences did not correlate with external fiber diameter.

2.2. Fiber selection and exposure media

The moisture media to which the spicule fibers and the melt-drawn glass fibers were exposed were seawater and distilled water. The saturation point was to be defined by soaking the sam-