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Effects of polar solvents on the mechanical behavior of fish scales

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ABSTRACT

Fish scales are unique structural materials that serve as a form of natural armor. In this investigation the mechanical behavior of scales from the *Cyprinus carpio* was evaluated after exposure to a polar solvent. Uniaxial tensile and tear tests were conducted on specimens prepared from the scales of multiple fish extracted from near the head, middle and tail regions, and after exposure to ethanol for periods from 0 to 24 h. Submersion in ethanol caused instantaneous changes in the tensile properties regardless of anatomical site, with increases in the elastic modulus, strength and modulus of toughness exceeding 100%. The largest increase in properties overall occurred in the elastic modulus of scales from the tail region and exceeded 200%. Although ethanol treatment had significant effect on the tensile properties, it had limited influence on the tear resistance. The contribution of ethanol to the mechanical behavior appears to be derived from an increase in the degree of interpeptide hydrogen-bonding of the collagen molecules. Spatial variations in the effects of ethanol exposure on the mechanical behavior arise from the differences in degree of mineralization and lower mineral content in scales of the tail region.

1. Introduction

Over the last decade there has been substantial effort placed on understanding the microstructure and mechanical behavior of selected structural materials in nature. The natural armors of the alligator, armadillo, fish, pangolin and others are excellent examples of materials in this category [1–9]. These materials have evolved to provide protection from outstanding threats without encumbering locomotion. While the "armor" of the aforementioned group of animals may appear disparate, they share the quality of most composite materials, i.e. they are constructed of a combination of constituents and possess mechanical properties superior to those of the individual components.

Elasmoid scales are found on teleost fish and have an interesting structure. In comparison to the bony or ganoid scales, elasmoid scales are relatively thin and compliant, which endow ease of movement to the fish. A number of studies have been conducted on elasmoid scales including those of the Carp (*Cyprinus carpio*) [6,7], Striped Bass (*Morone saxatilis*) [8,10,11], *Pagrus major* [12], and *Arapaima gigas* [1–3,13–15]. The structure of elasmoid scales is hierarchical and is composed of two primary layers (Fig. 1). The external or "limiting layer" is highly mineralized and consists of calcium-deficient apatite or calcium carbonate, depending on the fish [6,13,16]. The internal layer or "elasmodine" is a composite of type I collagen fibers and apatite mineral. The fibers are sparsely reinforced with mineral and organized in discrete plies, which are arranged in the form of a plywood structure. The diameter of the collagen fibers is near 1 μm, and they are constructed of an assembly of fibrils roughly 100 nm in diameter [2,6,10,11,16,17]. The individual fibrils and interfibrillar minerals of scales have been observed in evaluations performed with transmission electron microscopy and atomic force microscopy [1,6,16].

Elasmoid scales exhibit a strong mineral gradient across the thickness, which is reflected in the mechanical properties. There is a substantial reduction in the hardness and elastic modulus distributions from the exterior to the interior layers [4,13]. This gradient in properties plays an important role on the puncture resistance [11]. The limiting layer (LL) acts as initial barrier that dissipates energy by brittle fracture. The fracture propagates to the interface with the external elasmodine (EE), resulting in delamination. Once the LL and EE have undergone gross failure, further penetration is resisted by the internal elasmodine and a concert of mechanisms that are largely dependent on the collagen fibrils. Delamination between adjacent plies and fibrils is key to the fracture resistance of scales and bestows them with incredible notch insensitivity [10].

Due to the rather large organic content, the mechanical behavior of fish scales has been found to be sensitive to hydration. Ikoma et al. [12] evaluated the tensile properties of dehydrated scales of *P. major* and reported an elastic modulus and tensile strength of 2.2 ± 0.3 GPa and 93 ± 1.8 MPa, respectively. Scales of *A. gigas* exhibited an elastic modulus of 0.8 ± 0.1 GPa and tensile strength of 22.3 ± 3.9 MPa in the hydrated condition, which increased to 1.4 ± 0.2 GPa and 53.9 ±

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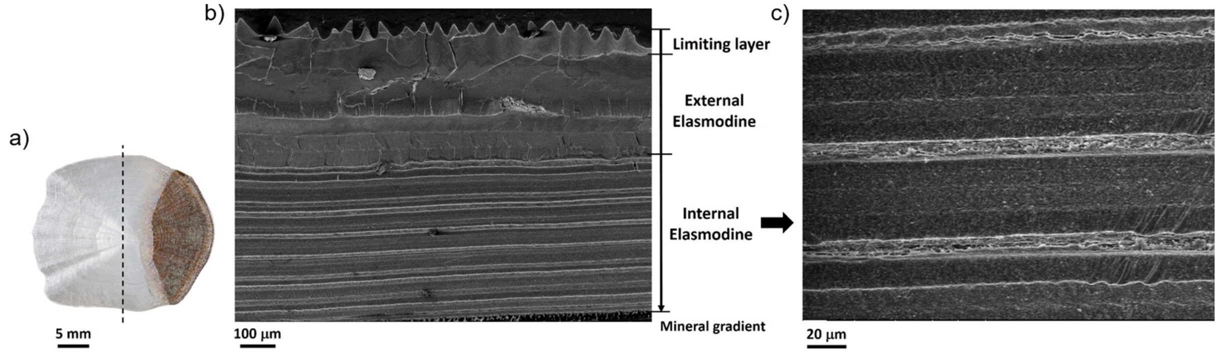

Fig. 1. Hierarchical structure of scales from the *Cyprinus carpio*. a) Individual scale with section line indicating the location of cross-section shown in (b) and (c). b) Highly magnified view of the scale structure across the thickness. Evident are the limiting layer at the surface of the scale, the external elasmodine and the internal elasmodine, which is located closest to the body of the fish. c) Ply distribution from a portion of the internal elasmodine.

8.4 MPa, respectively with dehydration [13]. Garrano et al. [6] found that the relative importance of hydration to the mechanical behavior of carp scales is a function of anatomical position. Scales from the tail underwent the greatest changes in performance with dehydration. One limitation of these previous evaluations is that dehydration was achieved by simple free convection in air. That process results in removal of the free water molecules, but requires substantial time and does not remove bound water [18–20]. Air-drying of *A. gigas* scales resulted in a residual water content of 16% in comparison to 30% for the hydrated scale [13].

Changes in the mechanical behavior with dehydration of collagen-based structural materials are at least partially related to the increase in interpeptide bonding with removal of the water molecules [18,19]. Dehydration of collagenous materials can be achieved by immersion in polar solvents, which displaces the water molecules residing within the collagen matrix with solvent and promotes hydrogen bonding between the peptide chains. Dehydration in this manner avoids other concerns related to dehydration in air. Therefore, the primary objective of this study was to evaluate the changes in mechanical behavior of teleost scales with exposure to polar solvents. A combination of uniaxial tension and tear tests was used to evaluate the changes in constitutive behavior and the resistance to fracture.

2. Materials and methods

Scales of the *C. carpio* (i.e. the common freshwater carp) were obtained by extraction from across the body of seven different fish after the methods of Garrano et al. [6]. These fish were marketed as East Asian carp, and no additional information was available for record. The scales were obtained nearly equidistant between the ventral and dorsal aspects of the body and from three regions including adjacent to the head, mid-length (beneath the dorsal fin) and near the tail (Fig. 2a). All of the scales were less than 1 mm thick and possessed a diameter that depended on the anatomical position. Scales from the head region had an effective diameter (d) ≥25 mm. Those obtained from the middle and tail regions ranged between 22 ≤ d ≤ 25 mm and

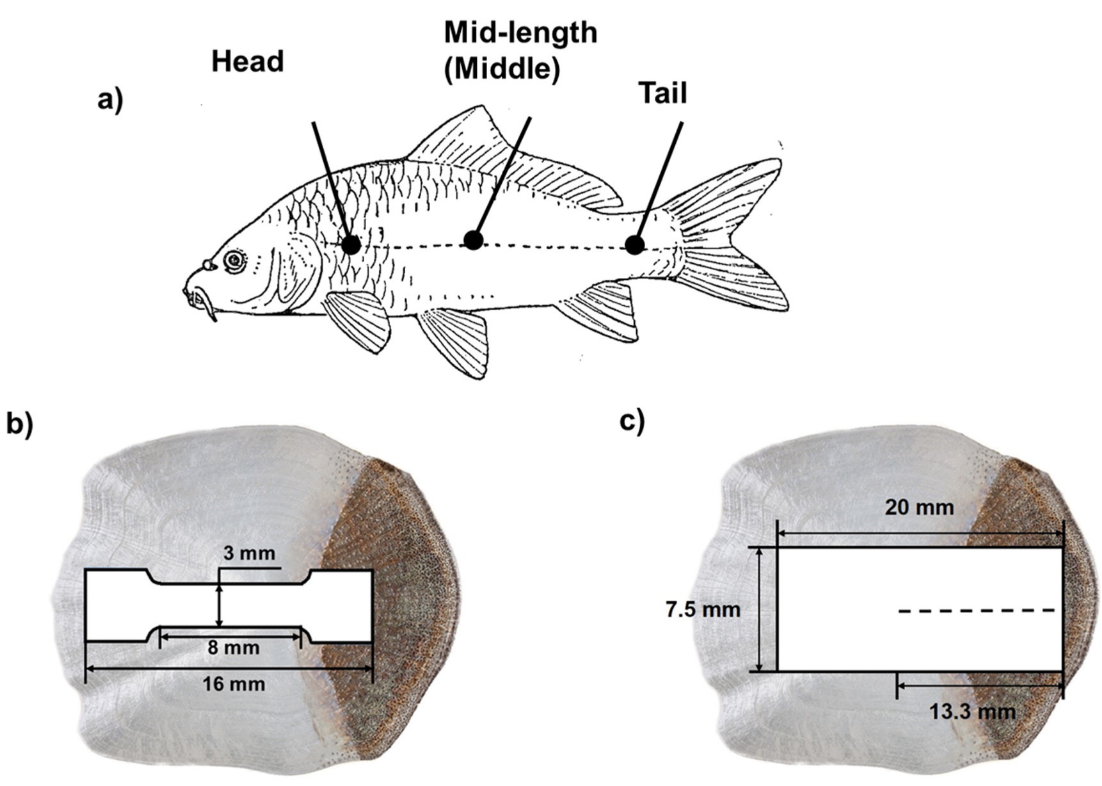

Fig. 2. Details regarding the specimens prepared for characterizing mechanical behavior. (a) Anatomical position of the extracted scales [6], (b) extracted scale with location and geometry of the stamped tensile specimens, and (c) geometry of the tear specimens.