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Research Paper

Teleost fish scales amongst the toughest collagenous materials

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ABSTRACT

Fish scales from modern teleost fish are high-performance materials made of cross-plies of collagen type I fibrils reinforced with hydroxyapatite. Recent studies on this material have demonstrated the remarkable performance of this material in tension and against sharp puncture. Although it is known that teleost fish scales are extremely tough, actual measurements of fracture toughness have so far not been reported because it is simply not possible to propagate a crack in this material using standard fracture testing configurations. Here we present a new fracture test setup where the scale is clamped between two pairs of miniature steel plates. The plates transmit the load uniformly, prevent warping of the scale and ensure a controlled crack propagation. We report a toughness of 15 to 18 $kJ\,m^{-2}$ (depending on the direction of crack propagation), which confirms teleost fish scales as one of the toughest biological material known. We also tested the individual bony layers, which we found was about four times less tough than the collagen layer because of its higher mineralization. The mechanical response of the scales also depends on the cohesion between fibrils and plies. Delamination tests show that the interface between the collagen fibrils is three orders of magnitude weaker than the scale, which explains the massive delamination and defibrillation observed experimentally. Finally, simple fracture mechanics models showed that process zone toughening is the principal source of toughening for the scales, followed by bridging by delaminated fibrils. These findings can guide the design of cross-ply composites and engineering textiles for high-end applications. This study also hints on the fracture mechanics and performance of collagenous materials with similar microstructures: fish skin, lamellar bone or tendons.

1. Introduction

Over millions of years of evolution, biological organisms have developed high-performance natural materials to fulfill a variety of structural functions. Materials like bone, teeth, scales or mollusk shells possess outstanding mechanical properties despite their relatively weak ingredients. During the past decade much research has been devoted to understanding the concepts, structures and mechanisms underlying the performance of these natural materials, so they can be implemented in high performance synthetic materials (Barthelat, 2007; Bonderer et al., 2008; Mayer, 2005; Studart, 2012; Mirkhalaf et al., 2014). Mollusk shells, arthropod cuticles, bone, teeth have already attracted a great deal of

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attention, and more recently many more natural materials have emerged as potential source of inspiration for new biomimetic materials (Meyers et al., 2008; Dimas and Buehler, 2012; Weaver et al., 2012). The structure and mechanics of natural scaled skin, and more particularly fish scales, have recently been the subject of several studies (Yang et al., 2013a,b; Bruet et al., 2008; Ikoma et al., 2003; Garrano et al., 2012; Lin et al., 2011; Meyers et al., 2012; Zhu et al., 2012, 2013; Browning et al., 2013; Zimmermann et al., 2013; Vernerey and Barthelat, 2010). Since their emergence 500 million year ago, fish have evolved scales with different shapes, sizes and arrangements which are generally classified into cosmoid, ganoid, placoid and elasmoid (Benton, 2004). Over the course of evolution the bony multilayered cosmoid and ganoid categories have largely been replaced by thinner yet more flexible teleost scales (Kardong, 2006). Natural scaled skins have remarkable mechanical properties: compliance, resistance to penetration, lightweight, and ultrathin structure (Yang et al., 2013a,b). Several studies on the structure and mechanics of fish scales were performed since on ancient bony scales (Bruet et al., 2008; Yang et al., 2013a,b) and on the more modern and lighter teleost scales (Ikoma et al., 2003; Garrano et al., 2012; Lin et al., 2011; Zhu et al., 2012). Mechanical characterization typically involved tensile testing (Ikoma et al., 2003; Garrano et al., 2012; Lin et al., 2011; Zhu et al., 2012) or indentation and puncture tests on individual scales (Bruet et al., 2008; Meyers et al., 2012; Zhu et al., 2012) or multiple scales (Zhu et al., 2013). Fish scales have also started to inspire new flexible protective systems (Browning et al., 2013; Chintapalli et al., 2014). Tensile tests on natural teleost fish scales confirmed the scale as a stiff, strong a tough material. In collagenous scales extensive inelastic deformation and energy dissipation were observed including pullout, defibrillation, sliding and rotation (Ikoma et al., 2003; Garrano et al., 2012; Lin et al., 2011; Zhu et al., 2012; Zimmermann et al., 2013). The function of the scaled skin is to provide protection while maintaining high compliance in flexion to allow for motion (Vernerey and Barthelat, 2010). One of the main functions of the scale is therefore mechanical protection against predators, collisions with other fish or obstacles or other mechanical threats. Recent studies have therefore focused on the indentation and puncture resistance of individual scales (Bruet et al., 2008; Zhu et al., 2012), showing that scales are superior to engineering materials such as polycarbonate and polystyrene (Zhu et al., 2012). This high performance can be explained by the ability of the material to dissipate large amounts of energy through large deformations. In turn, these large deformations are possible because the material can resist the propagation of cracks that could emanate from pre-existing defects in the materials and/or from high stress concentrations typical to puncture or laceration. In this context high fracture toughness becomes a desirable property, and early tests noted that indeed some fish scales are so tough that they could not be fractured, even after immersion in liquid nitrogen (Currey, 1999). Fracture tests on nonlinear, extensible and tough materials are in general difficult using traditional fracture testing configurations. For elastomers the "trouser" tear test circumvents some of the experimental difficulties (ASTM, 2003), and it is successfully applied on biological elastomers such as skin (Purslow, 1983). However, this test provides a mode III fracture toughness, which may differ from mode I fracture especially if fracture process is governed by defibrillation and fiber bridging as in fish scales. Instrumented mode I fracture tests on individual fish scales are extremely difficult because of their small size and high fracture toughness. To the best of our knowledge, toughness could only be measured on scales from gar, which are heavy ganoid scales with sufficient size, thickness and stiffness to permit toughness measurement in bending (Yang et al., 2013a,b). Gar scales were found similar to cortical bone in terms of composition, structure and fracture toughness (3 to 5 MPa $m^{1/2}$ (Yang et al., 2013a,b)). However it has so far been impossible to measure the toughness of teleost fish scales because there are thinner, smaller, and because they undergo massive inelastic deformation. The toughness of this type of scale appears to be so high that it is not possible to fracture them using conventional fracture test configurations. In this paper we demonstrate that teleost fish scales from striped bass (*Morone saxatilis*) are notch insensitive, an indication of high toughness. Using a new miniaturized fracture test setup we then report, for the first time, the fracture toughness of teleost scales from striped bass (*M. saxatilis*) along different directions. The fracture toughness of the bony layer, collagen layer and non-collagenous interfaces were also measured. We finally use a set of simple fracture mechanics models to assess the main contributors of the high toughness of fish scales.

2. The hierarchical structure of scales from striped bass *Morone saxatilis*

Like many other biological materials (Fratzl and Weinkamer, 2007), fish scales display a hierarchical structure organized over several length scales (Fig. 1) (Zhu et al., 2012). Individual scales of striped bass are roughly pentagonal in shape and about 8–10 mm in diameter. Topological features on the surface of the scale, together with the underlying microstructure define different sectors on the scale: anterior (A), posterior (P) and lateral (L) regions. The anterior region of scales exhibits a triangular shape with radial grooves (radii) and circular rings (circuli) forming around the central area of the scales called "focus" (Zhu et al., 2012). While radii are only present in the anterior field, circuli also appear in the posterior region but their circular form is not well recognized (Zhu et al., 2012). It is believed that radii promote the flexibility of the scales and circuli are involved in the anchoring of the scale into the dermis (Zhu et al., 2012). Scales are the thickest at the focus region (300–400 μm), and the thickness decreases continuously towards the edges. A cross section of the scale reveals two distinct layers: the outer layer which is partially mineralized (hydroxyapatite volume fraction of 30% (Zhu et al., 2012)) and often called "bony layer", and the inner layer which undergoes less mineralization (hydroxyapatite volume fraction of 6%) and is referred to as "collagen layer" (Fig. 1). Each layer is composed of approximately 10–20 plies each ~5 μm thick, which are composed of fibrils of collagen type I. Plies "R" are composed of fibrils aligned along the radial direction while plies "C" are composed of fibrils