MUSSEL BYSSAL THREADS AS AUTONOMIC AND INTRINSIC SELF-HEALING METALLO-POLYMERIC BIOFIBERS

Matthew J. Harrington[1], Admir Masic[1], Niels Holten-Andersen[2], J. Herbert Waite[3],
Peter Fratzl[1]

[1]Max Planck Institute of Colloids and Interfaces, Dept. of Biomaterials, Research Campus Golm,
Potsdam 14424, Germany.
Email: Matt.Harrington@mpikg.mpg.de

[2]University of Chicago, Dept. of Chemistry, Chicago, IL 60637, USA

[3]University of California Santa Barbara, Dept. of MCDB, Santa Barbara, CA, 93106, USA

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ABSTRACT

Biological systems offer insight into the design of self-healing materials. Bone mending and wound healing are often evoked as sources of bio-inspiration[1]; however, because these processes rely on complex cellular signalling cascades, the applicability of extracted design principles to technological applications is limited. Alternatively, through evolution, nature has generated several less prominent but equally remarkable biological materials, such as the mussel byssus, that are devoid of living cells and that nonetheless exhibit autonomic and intrinsic damage repair properties. Byssal threads are biopolymeric load-bearing attachment fibers secreted by marine mussels, which exhibit two noteworthy examples of acellular self-healing in the fibrous core and protective outer cuticle, respectively (Fig. 1a and b). Thread healing is an intrinsic property arising from aspects of the chemical structure and hierarchical organization of the biopolymeric subunits. Here, we discuss the relationship between the biochemical composition, hierarchical structure and mechanical performance of byssal threads. Results strongly suggest an integral role of metal-protein coordination complexes as reversible cross-links that mediate the healing behavior. Preliminary attempts to integrate these distinctive chemical concepts into polymers with self-healing properties have been successful.

Fibrous core: post-yield recovery in a tough and extensible biofiber

Byssal threads dissipate up to 70% of applied energy as mechanical hysteresis following material yield (Fig. 1c)[2]. Yield results in compromised mechanical performance during subsequent cycles, indicating damage to the material at the molecular level. However, if the thread is allowed to rest, the mechanical properties begin to recover (after one hour, the thread can heal to 70% of the initial performance)[2]. The composition of the core consists of protein[3] and a small amount of inorganic ions (~1% dry weight mostly Cu^{2+} and Zn^{2+})[4]. Core proteins are block copolymer-like with a large rigid central collagen domain and short domains at both ends rich in the amino acid histidine (up to 20 mol% locally) (Fig. 1c)[3]. The ability of histidine to coordinate metal ions and the co-localization of Cu^{2+} and Zn^{2+} in the core, led to the hypothesis that His-metal cross-linking is playing the role of a reversible sacrificial bond that ruptures during yield and reforms during healing (Fig. 1c). Several lines of evidence involving treatments aimed at disrupting His-metal coordination support this hypothesis[3, 4]; however, current work is focused on better characterizing these cross-links and determining the role of hierarchical organization.

Protective cuticle: extensible coating with controlled microcracking and healing

The outer cuticle of byssal threads has a knobby appearance resulting from hard granular inclusions embedded in a stretchy matrix and serves to protect the softer fibrous core from abrasive damage (Fig. 1b)[5]. This unlikely blending of hardness and stretchiness is difficult to achieve in current engineering polymers, but is apparently achieved in the cuticle through microcracking in the matrix between granules, which delays the onset of catastrophic failure of the cuticle (Fig. 1d)[5]. Furthermore, preliminary evidence suggests that microcracks self-heal after stretching. The cuticle is composed of a protein known as mussel foot protein 1 (mfp-1), which contains up to 20 mol% 3,4-dihyrdoxyphenylalanine (dopa) and elevated levels of iron[5]. Resonance Raman spectroscopy studies revealed a non-homogenous distribution of tris-dopa-Fe^{3+} coordination cross-links in the cuticle, such that the granules are cross-link dense islands in the less cross-linked matrix (Fig. 1d)[6]. Consequently, it was hypothesized that the microcracking behavior and subsequent healing was the result of reversible rupturing of dopa-Fe cross-links in the matrix, whereas, the high cross-link density granules provide the high hardness of the material. Therefore, the cuticle has lessons to provide not only on how reversible cross-links can result in self-healing behavior, but also about how different factors can be tuned to control how and where damage occurs. The dopa-Fe^{3+} cross-linking strategy that characterizes the byssus cuticle has recently been adapted to a synthetic analogue, producing a hydrogel with self-healing behavior[7]. The integrity of the gels has been shown to depend strongly on the degree of metal coordination, which was shown to be tunable using pH. These results suggest the potential for a biomimetic approaches in developing novel self-healing polymers.

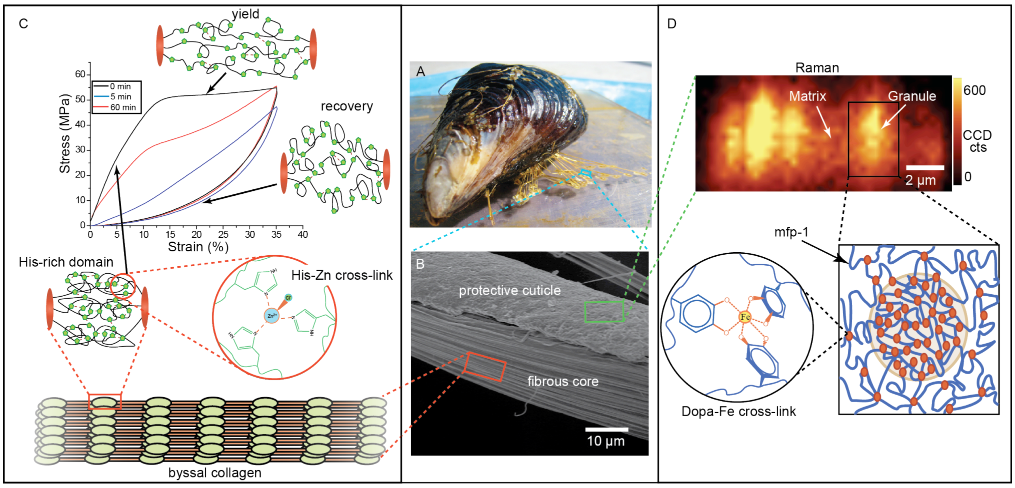

Figure 1. Byssal threads as self-healing shock absorbing fibers. (A) Mussels secure themselves to surfaces with byssal threads. (B) The fibrous core of the byssal thread behaves as a self-healing shock absorber and the protective cuticle acts as an abrasion-resistant coating. (C and D) Both core and coating owe their remarkable damage repair properties to hierarchical arrangements of protein-metal cross-links.

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