

SOFT, STRONG AND TOUGH MATERIALS, INSPIRED BY MUSSELS

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Marine mussels create an array of adhesive contacts (the byssus) to secure themselves to rocks, wood, metals and other mussels in the harsh conditions of the intertidal zone.¹ Their superb mechanical and adhesive performance has served as inspiration to create mussel-inspired materials for a wide range of applications ranging from surgical glues to primers and coatings.² Historically, much of this success has relied on mimicry of the molecular properties of the mussel's adhesive interfacial proteins, which are enriched in iron-binding catechol motifs, to create tough, but soft hydrogels.³⁻⁶ By contrast, the translation of the meso- to macro-scale properties of the natural materials has been comparatively unexplored, providing rich opportunities for further property enhancement to create durable, load-bearing materials. Here, I will present my laboratory's recent work characterizing the properties of natural mussel byssal plaques, and translating these discoveries to enable the design and manufacture of high performance materials.

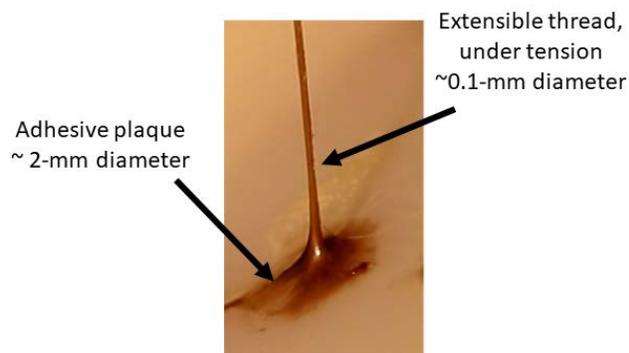


Figure 1: Image of surface-attached plaque under moderate tension. Photo credit: Younghoon Kwon and Justin Bernstein, UCSB.

To understand the origins of mussel adhesive performance, we first study the properties of the natural materials themselves. Mussels are found abundantly off the California coastline, and provide an excellent source of motivation and materials for this work. Experimentally, we collect *Mytilus californius* mussels (Conrad, 1837) from the fishing pier (34.415605, -119.828911) on the coast of Goleta, CA and place them in shallow tanks with continuously circulated and aerated raw seawater.⁷ Mussels are placed on glass substrates, upon which they deposit plaques (Figure 1), which are millimeter-scale acellular adhesive pads that are attached at the other end to the mussel body via a long and extensible collagen-rich thread. After deposition, the threads are cut, and the substrates with attached plaques are placed in Milli-Q water to maintain hydration until testing.

To observe the dynamics of mussel plaques as they debond from glass, we developed a custom built load frame with integrated dual view imaging capabilities, that enables measurement of plaque detachment dynamics under monotonic and cyclic loading.⁷ We pair these mechanical tests with ultrastructural analysis using scanning electron microscopy and neutron scattering to understand the molecular origins of strength and toughness.⁸⁻⁹ We found a robust mechanical response to load (Figure 2). At small extensions, a linear regime is observed and in this regime, no internal damage to the plaque material is seen. At larger deformations, the sample yields, and damage begins to accumulate within the plaque core, which consists of a disordered solid foam into which collagen-rich filament bundles extend from the thread. Damage, in the form of pore wall fracture, collagen scission and fiber:matrix delamination, serves to dissipate stress and avert the structural failure of the interface. At even higher loads, a second linear regime is observed. In this regime, large voids are present and growing within the plaque body, and damage begins to occur within the cuticle, a stiff coating that covers both the plaque and thread. Eventually, the structure fails, either through adhesive failure and delamination, or cohesive

failure of the plaque or thread. Such failures occur via different modes at similar forces, suggesting that the mussels have evolved an optimal force threshold for failure.

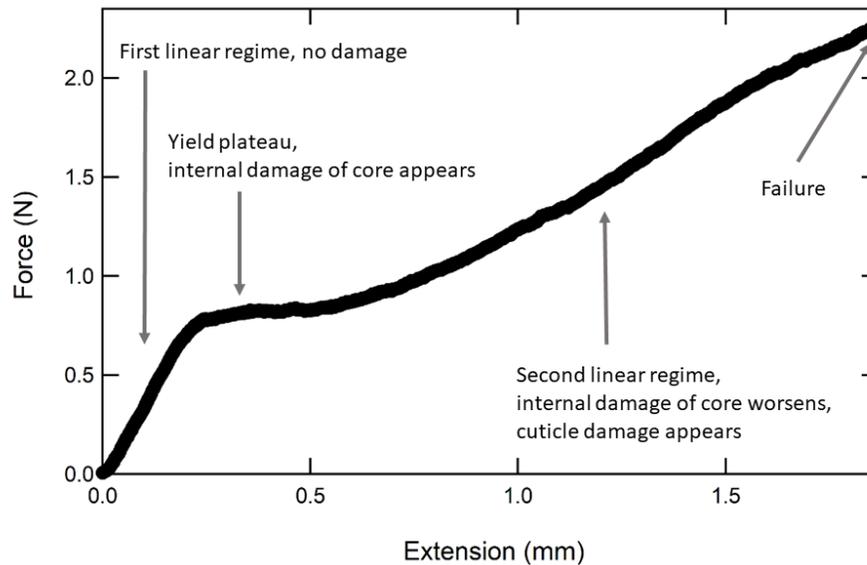


Figure 2: Representative force-extension curve for a ~2-mm diameter plaque, to which tension is applied through a short ~2-mm segment of thread.

Using insights from the natural system, we then create high-performance synthetic materials that are extremely strong and tough. By incorporating sacrificial, reversible iron-catechol cross-links into a dry, loosely cross-linked epoxy network, we recently demonstrated orders of magnitude increases in stiffness, tensile strength, and toughness compared to the iron-free precursor, without sacrificing extensibility.¹⁰ In a separate study, we showed that the addition of a nanoscopic catechol-based priming layer increased the adhesion strength of a crosslinked polymethacrylate resin on mineral surfaces by up to an order of magnitude when compared with conventional silane- and phosphate-based grafts.¹¹ In both cases, we demonstrated the utility of the mussel-based bonding chemistries in creating stiff, tough, load-bearing materials. In addition to these molecularly-engineered materials, we are also generating macroscale mussel-inspired 3D structures with tunable stiffness and strength using 3D printing approaches to better understand the important role of geometry and load distribution in maintaining adhesive strength.

In summary, the bioinspired approaches presented here offer tremendous advantages for materials development. By pairing biocompatible, non-toxic chemistries with advances in additive manufacturing and engineering design we are pursuing exciting new avenues for material optimization for broad applications ranging from packaging to soft robotics to tissue repair.

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