

Biomimetic Underwater Adhesives

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1. Introduction & Motivation

Designing adhesives that can maintain performance underwater is both interesting and important. Perhaps you have experienced the challenge of underwater adhesion firsthand if you've ever had a Band-Aid fall off while swimming or observed a piece of tape lose its tack when it becomes wet. Underwater adhesion is a very challenging problem that spans many formal disciplines including polymer chemistry, materials science, and mechanical engineering. A simple, scalable, robust material that can adhere to many types of surfaces in both dry and wet conditions could transform many industries including medical materials, underwater soft robots, and consumer products. Imagine a surgical device that could be applied to a ruptured vessel and immediately stop bleeding. However, to date, many synthetic polymers and materials design principles used to develop dry adhesives translate poorly to the development of underwater adhesives. Fortunately, many marine organisms including the blue mussel (*Mytilus edulis*) have evolved highly specialized proteins that exhibit robust underwater adhesion to diverse substrate compositions in many different applications. These proteins serve as a valuable starting point to leverage principles of biomimicry in the design of next-generation underwater adhesives. This presentation will identify the origins of biomimicry in the design of underwater adhesives and highlight recent advances in this rapidly growing field. Emerging topics and potential applications will also be discussed.

2. Foundations of Biomimicry in Underwater Adhesives

Initial efforts to explore the unusual adhesive capabilities of marine organisms date as far back as the late 1980s when Waite et al discovered high concentrations of catechol-bearing dopa residues in specialized proteins secreted by the blue mussel.¹ These proteins, termed mussel foot proteins (mfp), exhibit robust adhesion to many materials found in the marine environment including organic matter and ceramics. Dopa residues are present in some types of mfp at concentrations up to 30 mol%. Dopa groups are thought to increase adhesion by creating many interfacial bonds including hydrogen bonds, coordination bonds, and van der Waals interactions through [pi]-[pi] stacking. The precise mechanisms by which Dopa-bearing materials increase interfacial bonding and improve interfacial adhesion continue to be elucidated and remain an active area of research. Based on many of these initial findings, Dopa motifs have been incorporated into many types of macromolecules including synthetic polymers, engineered proteins, and films such as polydopamine.^{2,3} Dopa may also work synergistically with other groups in mfp to greatly improve the underwater adhesion of these materials.⁴ Recent findings also suggest that improved underwater adhesion relies upon synergistic interactions between Dopa groups and other motifs in mfp including redox active metals and flanking cationic amino acid residues.⁵ The diverse composition afforded by mfp combined with many possible synergistic interactions produce complexity, but also offer many opportunities to inform the biomimetic design of underwater adhesives using computational approaches, for example.

3. Emerging Topics and Applications of Biomimetic Underwater Adhesives

The design, synthesis, and testing of biomimetic underwater adhesives is a comparatively mature field in the context of polymeric biomaterials research. Yet, many fundamental scientific questions persist and many technical challenges remain. Perhaps the most compelling question yet to be answered is the following: What governs the practical limit of the performance of an underwater adhesive? A comprehensive understanding of this subject could inform the design

of next-generation adhesives. There are many other intriguing research directions for underwater adhesives including: the design of stimuli-responsive materials; polymers that can exhibit reversible or adaptive adhesion; integrating nano- or microstructures to improve adhesion; incorporating energy-dissipating motifs; exploring materials synthesized by marine organisms that exhibit unusual adhesive or cohesive properties. In addition to fundamental research, there are many challenges and opportunities in technological translation including scalable materials synthesis, interfacial fouling, and adhesion in complex environments. This presentation will highlight select applications for underwater adhesives including use as a hemostatic medical material and as a substrate for transfer printing of flexible hydrogel-based electronics.^{6,7}

4. Conclusions and Outlook

Bioinspired materials for underwater adhesion is a decades old field that has benefited from concurrent advances in adhesion science, polymer science, macromolecular engineering, and advanced instrumentation. The initial phases of biomimetic materials design have incorporated dopamine-based motifs in various configurations to produce high performance adhesives that function effectively in aqueous conditions. There is great commercial and economic potential in translating this broad class of materials. However, many challenges and opportunities for next-generation underwater adhesives remain.

References

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