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Advanced surfaces enrich the high-throughput engineering of physical and chemical phenomenon (e.g., electrical, magnetic, electronics, thermal and optical controls), large surface area, protective coatings against water loss and excessive gas exchange, etc. A more sophisticated example could be a highly selective surface permeability allowing passive diffusion and selective transport of molecules in the water or gases. Smart surface technology provides an interlayer model which prevents the entry of substances without affecting the properties of neighboring layers. A number of methods have been developed for coatings, which are essential building blocks for the top-down and/or bottom-up design of numerous functional materials. They own exclusive surface features in terms of new age device applications. This book, Advanced Surface Engineering Materials, offers detailed up-to-date chapters on functional coatings and adhesives, engineering of nanosurfaces, high-tech surface, characterization and new applications.

With the increasingly deep integration of present and emerging surface engineering technologies for new materials exploration, the last decade has witnessed an inspiring growth in research activities involving multidisciplinary knowledge innovation, some of which have already activated further market demand. Advanced Surface Engineering Materials, part of the “Advanced Materials Series”, provides a wide spectrum of readers with an overview and systematic knowledge of the aforementioned categories. With such a book in hand, one can easily figure out the methodology and essential rationales underlying every aspect of material innovations—from bio-inspired coating or polymer films to biosynthesis of nanomaterials and graphene, from carbon structures growth to deep-blue organic light-emitting diodes, or from latent biosensor application to high efficiency devices assembly—and the topic can be extended even to the modulation of enzymes or the assessment of plasma-material interactions for process safety. As a whole, this book constitutes a state-of-the-art review of the advances in surface engineering materials science and technology.
This book is written for readers from diverse backgrounds across the fields of chemistry, physics, materials science and engineering, medical science, environmental, bio- and nanotechnologies, and biomedical engineering. It offers a comprehensive view of cutting-edge research on surface engineering materials and their technological importance.

We would like to express our gratitude to all the contributors for their collective and fruitful work. It is their efforts and expertise that have made the monograph comprehensive, valuable and unique. We are also grateful to Drs. Sachin Mishra and Sophie Thompson, managing editors of the Advanced Materials Series, for their help and useful suggestions in preparing this book.

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Part 1

FUNCTIONAL COATINGS
AND ADHESIVES
Bio-inspired Coatings and Adhesives

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Abstract

Biological organisms such as marine mussels have attracted attention as a paradigm of strong and versatile adhesion to hard surfaces under the severe chemical and physical environments of the wave-swept shores. Recent studies to understand the molecular mechanisms and mechanochemical aspects of mussel foot protein adhesion to different substrates have inspired the development of a variety of underwater adhesives, strain-resistant materials, hydrogels, self-healing polymers, and surfactants for tissue repair, drug delivery, anti-fouling coatings, and medical adhesives applications. In this chapter, we start to systematically discuss the physicochemical process at the molecular level during the attachment of mussel plaque to a substrate followed by the role of different amino acid residues in the attachment process. We then provide fundamental insights into the molecular architecture–function relationship for synthetic bio-inspired adhesives as well as begin to develop design principles for bio-inspired wet adhesives. This is followed by a thorough review of the recent development in mussel-inspired underwater polymer adhesive coatings and surfactant nano-adhesives that emphasizes the importance of the balance between electrostatic and hydrophobic interactions for wet adhesion and coacervation in addition to catecholic interactions, e.g., oxidative cross-linking, metal coordination, and intermolecular hydrogen bonding. We also shed light on intermolecular hydrogen bonding for surface-initiated underwater self-healing of polymers and metal-mediated cross-linking inspired from the mussel threads that provide sacrificial and reversible bonds at interfaces for strain-resistant materials.

Keywords: Mussel, wet, underwater, adhesives, coatings

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1.1 Introduction

Nature has developed surprisingly elegant and diversified adaptations for the survival of the fittest organisms by a smart control of the interfacial forces and regulating surface interactions with the surroundings. For instance, geckos can cling and run with impeccable dexterity on most surfaces regardless of its roughness by controlling the frictional adhesion [1, 2] between its hierarchical fibrillar structures on the footpad and the surface. They avoid slip [3] during sticking and shearing of the nanosized spatula on a surface and employ van der Waals’ forces [4] to adhere to dry surfaces. Similarly, tree frogs that reside in the arboreal habitat of the wet rainforests take advantage of the capillary and viscous forces to prevent it from falling while running on surfaces [5, 6]. Currently, researchers in the wet adhesion community are spearheaded to solve the engineering challenge of wet underwater adhesion through mimicking techniques employed by the marine organisms such as barnacles [7, 8], pearl oysters [9, 10], minicollagens from sea anemones [11], sandcastle worms [12, 13], and the marine mussels [14, 15].

Harsh intertidal oceanic waves are no match for the mighty mussel that produces strong, flexible threads and cling to the surfaces of rocks, piers, and boats and even to other mussels without getting washed by the impact of water. This extraordinary ability of the mussels to adhere to any surface underwater has been baffling researchers for the past few decades. The adhesion mechanism used by the marine mussels has been extensively explored recently, and efforts have been made to develop coatings and adhesives for a variety of applications ranging from dental adhesives [16], self-assembled bilayer nano-adhesives [17], antifouling surfaces [18], self-healing polymers [19], drug delivery chaperons [20], medical glues [21], etc. Understanding the technique used by the mussels to prepare the surface for adhesion and the molecular mechanism underpinning the adhesive strength of the mussel glue (i.e., the mussel foot proteins or mfps) is fundamental to design synthetic mimics of the biological system.

1.2 The Interfacial Biochemistry of a Mussel Adhesive

Marine mussels are experts at ‘wet’ adhesion, achieving strong and durable attachment to a variety of surfaces in their marine habitat. Adhesion is mediated by a byssus, essentially a bundle of leathery threads that emerge from living mussel tissue at one end and tipped by flat adhesive plaques at the other (Figure 1.1). The byssal plaques consist of a complex array
of proteins (mostly six different mussel foot proteins, mfps 1–6), each of which has a distinct localization and function in the structure, but all share the unusual amino acid 3,4-dihydroxyphenylalanine (Dopa), a post-translational modification from tyrosine (Tyr or Y), that features prominently in mfps, ranging from less than 5 mol% in mfp-4 to 30 mol% in mfp-5 [24–29]. Mussels use its foot to make a snug contact with a target surface prior to depositing adhesive mfps in a fashion resembling injection molding [30]. The dimpled distal depression of the foot is positioned over a surface like an inverted rubber cup and compressed, thereby pushing out bulk water. Mfps are then secreted into the remaining gap from 8 to 10 pores in the depression ceiling [31].

Strong and durable adhesion is achieved despite the surrounding seawater at pH 8.2, high salt and saturating levels of dissolved O₂. The interfacial pH at which mussels buffer the local environment during mfp deposition was determined using a pH-sensitive surface (e.g., mica functionalized with a fluorescent bilayer) to range from 2.2 to 3.3, which is well below the seawater pH of 8 [14]. The mussel foot significantly acidifies the interface during initial protein deposition (Figure 1.2). The role of acidification is to retard the oxidation of Dopa residues in the mfps for the formation of hydrogen bonds, metal–catechol coordination, or cation–π interactions.
with the surface to secure the proteins/plaque to the substrate. Deposition of adhesive proteins at acidic pH has important implications for mussel-inspired technology. The acidic pH allows delivery of the mfps to a surface as complex coacervate fluids; together with antioxidants [32], stabilizes the catecholic residue in the protein enabling the formation of electrostatic bonds with a mineral surface or coordination bonds with the surface oxides; favors the formation of cationic functionalities, e.g., Lys, Arg, and His for long-range attraction to electronegative surfaces. The acidic pH in combination with seawater (pH 8.2) serves as a switch for initiating
protein insolubility, quinone-based cross-linking and catechol-mediated metal chelation (Figure 1.3).

The oxidation of Dopa to quinones and related products is highly favorable under high-pH conditions of the seawater and undermines
the strength of protein adhesion to mineral surfaces [32, 33]. The acidic pH micro environment used by the mussels was proposed to limit mfp-Dopa oxidation, thereby enabling the catecholic functionalities to adsorb to surface oxides and provide a solubility switch for mfps, most of which aggregate at pH ≥ 7–8 [14] (Figure 1.3).

The mussel foot proteins, mfp-1, a coating protein [34] and, adhesive mussel foot proteins, mfp-3 [22] and mfp-5 [35], have been shown to exhibit remarkable binding to mineral surfaces such as mica, TiO$_2$ [34, 36], and collagen [22], a biological protein that is abundant in bones, muscles, skin, and tendons, where it forms a scaffold to provide strength and structure. The versatility of mussel adhesion to surfaces with wide-ranging chemical and physical properties has inspired much research dedicated to understanding the mechanism of mussel adhesion as well as developing biomimetic coatings and adhesives for wide-ranging industrial and biomedical applications, the latter including paints for coronary arteries [37], fetal membrane sealants [38], cell encapsulants [39], and for securing transplants for diabetics [40].

Several studies with Dopa-functionalized polymers have demonstrated a strong positive linear correlation between Dopa content and adhesion to different surfaces [41–45]. In fact, the binding ability of the mfps to different substrates thus has been mostly attributed to the Dopa functionality in the protein, and the role of the other peptide residues in the adhesive properties of the protein remains elusive. Mfps such as mfp-3 [22] and mfp-5 [35] contain 20–30 mol% Dopa and are highly adhesive (e.g., adhesion energy, $W_{ad} \approx 8 \text{ mJ/m}^2$ for mfp-3 to $\sim 14 \text{ mJ/m}^2$ for mfp-5 on mica) within narrowly defined solution conditions, e.g., low salt <150 mM ionic strength and pH~3–5. However, more recently, it was demonstrated that the adhesion (interaction of the protein with a different substrate) and cohesion (self-interaction between the proteins) of mfps is independent of the Dopa residues in the protein [46]. It was proposed that the mfps adhere to mineral surfaces through cation–π interactions between the aromatic residues in the protein and cations (e.g., potassium ions) adsorbed to the mineral surface rather than bidentate hydrogen bonding (Figure 1.4) [46]. This is a paradigm shift in our understanding of the molecular mechanisms underlying the adhesive properties of mfps and calls for further inquiry into the effects of peptide residues beyond Dopa chemistry.

A strongly bound stable hydration layer to a surface and/or adhesive polymer (or molecule) is thought to be a potential barrier that averts reliable adhesion of the polymer to the surface. Recently, dynamic nuclear polarization technique was used to demonstrate that hydrophobicity in the mfps mediates dehydration at substrate protein interface to allow
force-free adhesion of the protein to a substrate mediated by Dopa [47]. It was also proposed that Dopa expedites the kinetics of bonding interactions between proteins and surfaces [46] or between polymers under wet environment [19]; however, the eventual strength of adhesion to a surface is more dependent on an optimal balance between the hydrophobic and electrostatic residues in the material [17, 48]. For instance, common amino acids, for example, cationic residues (lysine, K; histidine, H), anionic residues (aspartic acid, D), nonionic polar residues (asparagine, N), aromatic residues (tyrosine, Y; tryptophan, W), and nonpolar residues (alanine, A) are relevant to mfp adhesion and their role in wet adhesion of proteins and synthetic polymers are under increasing scrutiny. Synthetic polymers mimicking the properties of these other aromatic residues with an optimal balance between these different functional residues along with Dopa have recently been incorporated into polymers to achieve the strongest underwater adhesion to date for mussel-inspired polymer adhesives [48].
The adhesion of the natural and recombinant mussel foot proteins has been studied onto substrates other than mica such as collagen [22], silica [23, 49], silicones [23], and titania [41, 50], which are more relevant to biomedical applications. Single-molecule tensile tests using an atomic force microscope (AFM) where Dopa was tethered to a cantilever tip showed that Dopa contributes to nano-Newton adhesion on iron oxide, titania, and amine-functionalized surfaces [51]. The force–distance profiles and adhesion energies of mussel foot protein 3 (mfp-3) to TiO$_2$ surfaces were measured at three different pHs (3, 5.5, and 7.5) using a surface forces apparatus (SFA) [50]. At low pH (3), mfp-3 showed the strongest adhesion force on TiO$_2$, with adhesion energy of $\sim 7.0$ mJ/m$^2$. Increasing the pH gives rise to two opposing effects: (1) increased oxidation of Dopa, thus decreasing availability for the Dopa-mediated adhesion, and (2) increased bidentate Dopa–Ti coordination (Figure 1.5), leading to the further stabilization of the Dopa group and, thus an increase in adhesion force. Both effects are reflected in the resonance-enhanced Raman spectra obtained at different deposition pHs. The two competing effects give rise to a higher adhesion force of mfp-3 on the TiO$_2$ surface at pH 7.5 than at pH 5.5.

Mfps have an intriguing potential for repair of collagenous tissues and serves as an inspiration for the design of medical glues. In the byssal attachment, mfp-3 mediates adhesion between the collagens of the thread on one side and a foreign surface on the other (Figure 1.1). The adhesive mfps also

![Figure 1.5](image) Possible modes of Dopa (catechol) binding to non-hydrated TiO$_2$ surfaces. The catechol group can form molecular adsorption with (a) two hydrogen bonds, (b) monodentate adsorption with one hydrogen bond and one coordination bond, and (c) bidentate adsorption with two coordination bonds, although which form the Dopa binds to a TiO$_2$ surface depends is pH dependent: at lower pH (<5.5), the molecular adsorption is preferred, and at higher pH (>7), the coordination charge transfer is more favorable. As marked, the red atoms are oxygen and the blue ones are titanium. (d) A summary of the adhesion energies of mfp-3 on TiO$_2$ in different pH buffers. The adsorption of Dopa on TiO$_2$ surface is highly pH dependent. At low pH, the protonated Dopa predominates, whereas at pH 7.5, there exists a mixture of both half- and fully deprotonated catecholates. This figure has been adapted from Ref. [50].