

Barnacle Adhesion Two-Step

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Prologue: Hard foulers such as barnacles compromise Navy ship hulls and other underwater surfaces, significantly increasing drag and fuel consumption of deployed ships. Increased maintenance of coatings and components due to fouling, as well as pressure to develop less toxic paints and surface treatments, motivates research into how foulers adhere in order to inform future coating development and antifouling strategies. Barnacles are among the most pervasive foulers, curing their insoluble adhesive underwater. The details of the curing process remain elusive due to the inherent challenge of the “buried” bonding interface underneath the barnacle.

NRL has established a multidisciplinary research team combining expertise in chemistry, biology, and materials science to study barnacle glue under living barnacles. The research team has discovered barnacle adhesion involves sequential secretions under the organism’s expanding periphery. Barnacles repeat this cycle throughout their lives, constantly adhering to the substrate as they expand to cover new territory. The team devised a way to reattach adult barnacles to clean,

petitive, timed movements or music’s adagio and allegro tempos, barnacle adhesion is accomplished sequentially: first by understated movement, then followed by a burst of activity. The majority of the growth (the big step or adagio-like movement) accomplishes half the adhesion, while a faster event (a short, quick step or allegro movement) quickly doubles the adhesive strength.

Step One — Adagio: Watching barnacles grow, like watching paint dry (or literally glue curing), is a slow process. Barnacles grow radially about one to two microns per hour, creating a set of rings that resemble the growth rings seen on a tree stump. For perspective, it would take a barnacle 30 to 60 hours to grow a ring as wide as a single strand of human hair. To speed things up, the team uses young barnacles and time-lapse photography under a microscope to watch the barnacles grow and develop their adhesive interfaces.

The barnacle grows larger by nearly continuously expanding and lengthening the side shell plates to create more volume inside the shell for the barnacle body and a larger diameter at the base where it adheres. While the process of advancing the perimeter is slow, the barnacle periodically develops some interesting features at the interface. During the slower, “adagio” growth, new capillary structures appear, extending ductwork and output ports that drain into the interface (Fig. 1, top). In young, fast growing barnacles, this repetitive process occurs every three days. However, the barnacle spends most of that time advancing the side plates, while the capillary ductwork appears well behind the leading edge of growth and becomes visible over a period of less than an hour.

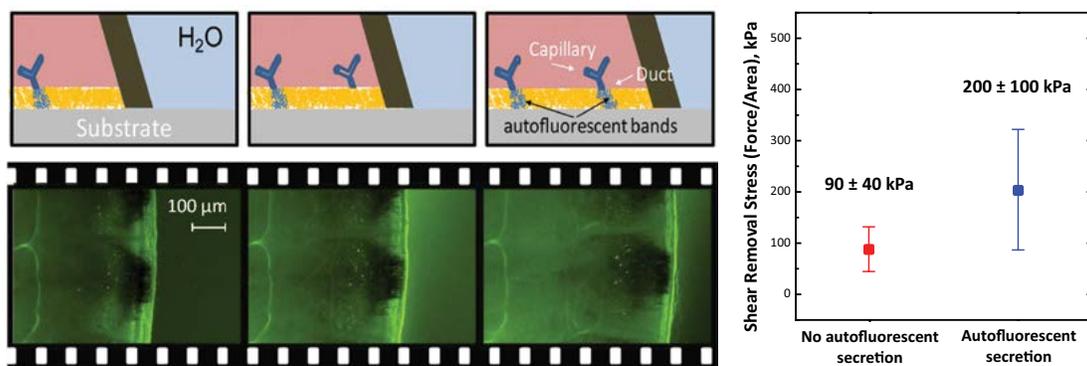


FIGURE 1

Cartoon depicting expansion of barnacle as viewed from the side (upper panels, left) and as viewed from below an actual barnacle through glass with UV illumination (lower panels, left). The base expands, and subsequently a new set of capillaries forms, secreting an autofluorescent fluid into the interface. Barnacles (*Balanus amphitrite*) removed from substrates before (right, red data) and after (right, blue data) the autofluorescent secretion show marked differences in the removal stress, which is nearly doubled after the capillary autofluorescence appears.

transparent substrates to monitor adhesion strength throughout the cycle. Watching the process from underneath, the team found that barnacle adhesion is a sequential, two-step process. Not unlike a dance’s re-

Step Two — Allegro: It has long been recognized that the capillary ductwork and the glands from which they originate play a key role in barnacle adhesion. The team was able to follow the development and secre-

tory activity of the capillaries using time-lapse, high-resolution optical microscopy under ultraviolet (UV) or “black light” illumination. The growing edge of the barnacle is semitransparent, and many of the structures within the barnacle light up under UV illumination in a process called autofluorescence. The capillaries are particularly bright (Fig. 1), and time-lapse photography reveals that these capillaries secrete an autofluorescent material over a short window of time (hours) at the end of the long adhesion cycle (days). Adhesion was measured before new capillary structures were visible, and doubled after the autofluorescence was detected. This experiment demonstrated that the second, quick step, identifiable by its bright autofluorescence, has a surprisingly powerful impact on adhesion (Fig. 1).¹

Finale: The experiments include novel approaches to reveal the detailed structure and chemistry of the interface components associated with increased adhesion,^{1,2} as shown in Fig. 2. The structures and chemistries involved in the interface building process are related to molting in invertebrates — the process by which barnacles, crabs, lobsters, and all other crustaceans shed their exoskeletons to enlarge their protective shells. In barnacles, part of this process occurs

underneath the shell where the barnacle adheres; this material cannot be discarded as in the normal molting process and thus is unique to barnacles. This work adds for the first time an analysis showing how multiple secretions, separated temporally and spatially underneath the living barnacle, combine to increase tenacity of barnacles to marine surfaces. Much work remains to identify the composition of these fluids and the chemistries involved. However, the results to date point to the importance of determining how growth and development impact adhesion in these pervasive foulers, as well as assist in guiding development of more effective, nontoxic surface treatments to prevent barnacle fouling.

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References

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- ² D.E. Barlow and K.J. Wahl, “Optical Spectroscopy of Marine Bioadhesive Interfaces,” *Annual Reviews of Analytical Chemistry* **5**, 229-251 (2012).

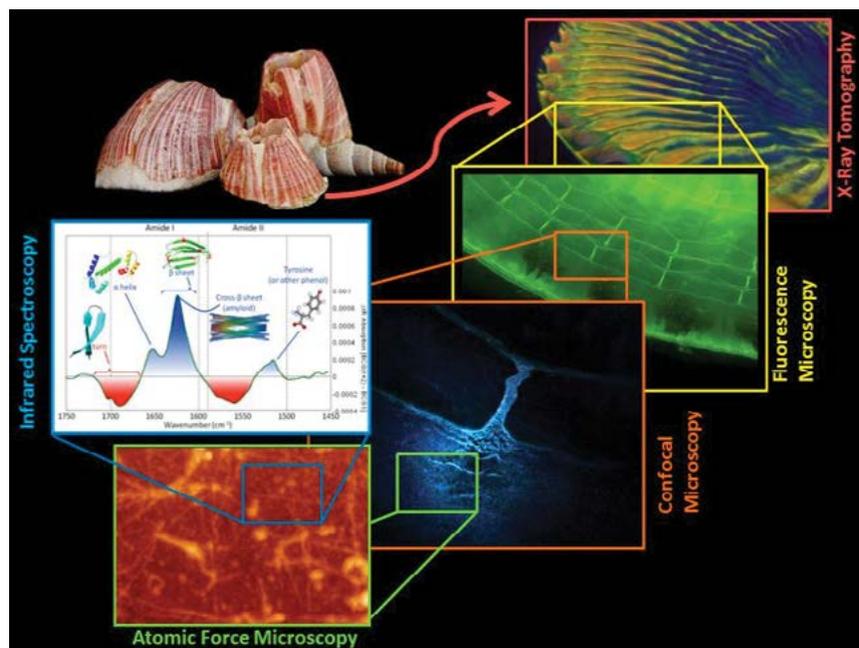


FIGURE 2

We use a multiscale, multiwavelength approach to determine how barnacles adhere to surfaces and the structures and chemistries responsible for adhesion. The structure of a barnacle shell (upper left) is examined by computer-aided X-ray tomography (CAT scan) (upper right). Barnacle growth and adhesion proceeds by expansion of the base and secretion of multiple fluids, a fraction coming from micron-scale capillary structures that form periodically underneath the barnacle. Fluid from the capillary structures autofluoresces (central images) and contains nanoscale fibrillar structures (lower left). Chemical analysis (middle left) reveals features consistent with fibrillar proteins and aromatic (carbon-ring structured) molecules.

Pulsed Electron Beam Driven Chemistry

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The Concept: We are studying the use of high energy pulsed electron beams to efficiently drive chemical processes. Practical applications include pollution control and the synthesis of fuels. The latter, if successful, could help meet both Navy and civilian energy needs, as it might lead to an efficient means to provide liquid fuels for existing Navy ships and aircraft as well as civilian transportation systems. At the most fundamental level, chemical processes require breaking apart the chain of one or more types of molecules and then allowing the constituents to recombine to another. Most chemical reactions require external energy, usually in the form of heat. When carried out in practice, this leads to large systems requiring high temperatures and pressures, and sometimes catalysts. A more efficient means of breaking chemical bonds is to deposit the energy with an energetic particle, such as an electron beam.¹ This is called electron beam radiolysis.

Advantages of a Pulsed Beam: Almost all chemical synthesis involves multiple steps. The initial bond-breaking takes only a few tens of nanoseconds (10 billionths of a second), whereas the subsequent recombination takes much longer. Thus, it is desirable to have the electron beam “on” long enough to break the bonds, but then “off” so as not to interfere with the recombination. Since one wants to break as many

bonds as possible, this calls for a high power, very short duration, electron beam. To be practical, the system must be capable of efficiently running at several pulses per second for long periods of time.

NRL Pulsed Electron Beam Science and Technology: The NRL Plasma Physics Division is developing the science and technology needed for just such a system. The NRL Electra facility (Fig. 3) generates a 500 kV, 100 kA, 100 ns, repetitively pulsed (5 Hz) electron beam and deposits its energy into a gas.² The peak power is 5×10^{10} (50 billion) Watts. Electra was originally developed to pump a krypton fluoride laser for inertial fusion energy. Our research has led to a system that operates at 5 Hz for several hours with a projected efficiency (wall plug to electron beam energy deposited into the gas) of greater than 60%. The present duration limit is due to the high voltage “spark gap” switches in the electron beam power supply. Just like their more common automotive spark plug cousins, these switches erode in time, leading to erratic performance. However, we have recently developed a prototype, all solid-state, pulsed power system that has run continuously for 11 million pulses at 10 Hz (319 hours). The individual components have been tested to at least 300 million pulses.

Conversion of Natural Gas and CO₂ to Liquid Fuels and Basis for Syngas: In one experiment, we irradiated a mixture of 10% CH₄ and 90% CO₂ with 500 electron beam pulses. The deposition per pulse was 0.08 J/cc. The gas constituents were measured before and after exposure using a residual gas analyzer (RGA). As shown in Fig. 4, we converted some of the carbon dioxide, a greenhouse gas, into hydrogen and CO, the basis of Syngas, and methanol, a cleaner burning liquid fuel.

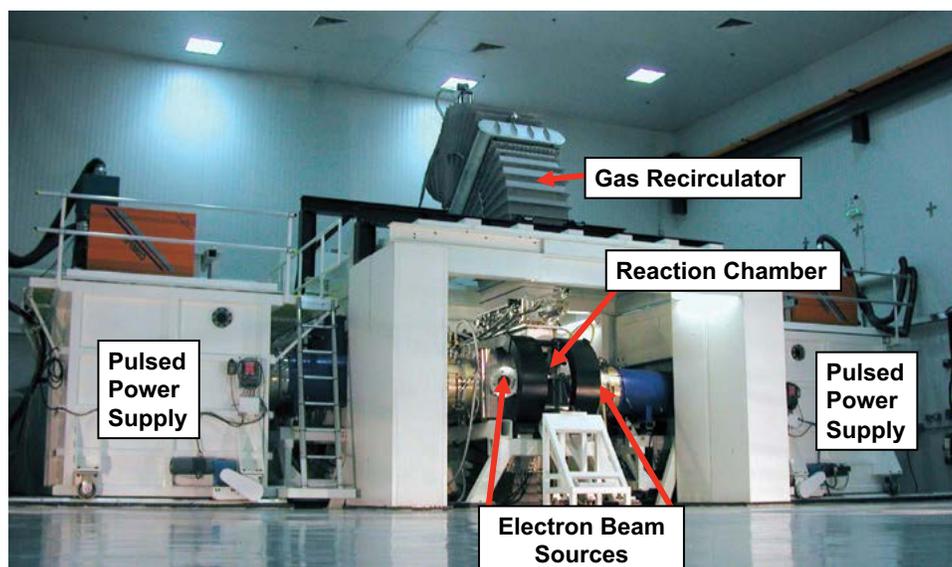


FIGURE 3
The NRL Electra Electron Beam Facility.

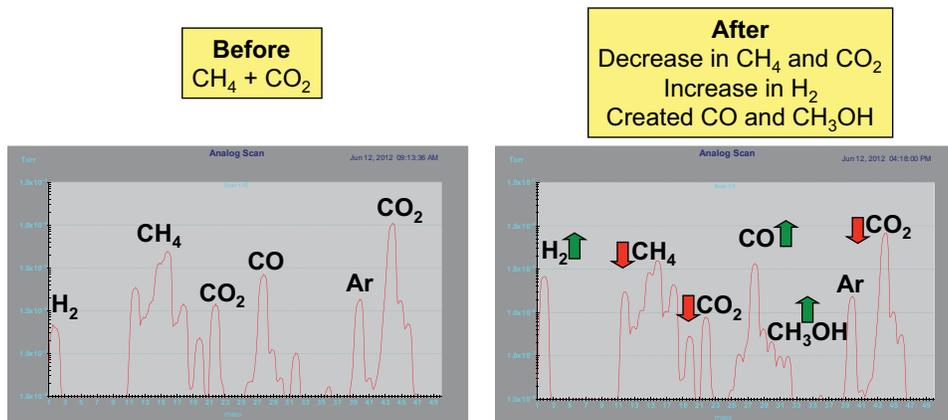


FIGURE 4 Residual gas analyzer of chamber constituents. Left, before; right, after. The data shows a conversion of a mixture of 10% natural gas CH₄ and 90% CO₂ to hydrogen and CO (Syngas), and methanol (CH₃OH).

Conversion of NO_x from a Coal Power Plant

Exhaust to Nitrogen and Oxygen: We have also shown that the electron beam can efficiently convert NO_x to nitrogen and oxygen. NO_x (mainly NO and NO₂) is a major source of acid rain and is found in the exhaust of any hydrocarbon-based power plant, be it fired by coal, oil, or even natural gas. Our experimental results are shown in Table 1.

References

- ¹R.A. Lee, "Febetron Radiolysis of CO₂ in the Presence of Oxygen and Carbon Monoxide," *Radiation Research* 77(2), 233–241 (1979).
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TABLE 1 — Conversion Results

Initial NO _x (ppm)	Final NO _x (ppm)	Removal efficiency	Electron beam deposition (J/cc)
500	9.91	98%	.084

The electron beam converted 98% of the NO_x to nitrogen and oxygen. The remaining concentration is below the current EPA requirements for power plant emissions.

Summary: There are many more applications for chemical reactions induced by pulsed electron beams. All would be optimized by a better understanding of the fundamental e-beam physics and chemistry. We are just starting to scratch the surface of this scientifically rich and diverse field.

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