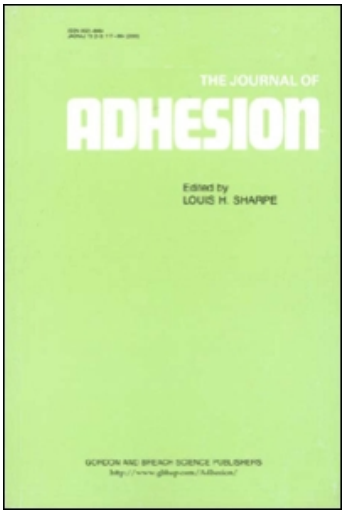

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Observations of Barnacle Detachment from Silicones using High-Speed Video

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Observations of Barnacle Detachment from Silicones using High-Speed Video

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The detachment of barnacles (under shear and tensile loads) from silicone was investigated with the aid of high-speed digital video recording. A handheld probe was used to apply loads to the shells of barnacles attached to three clear silicone-elastomer coatings of known thickness applied to glass plates. The tests were performed in the laboratory in air and underwater. Representative data are presented as a qualitative description of separation at the barnacle adhesive–silicone interface. Detailed examination of adhesive separation during detachment provided new insight into the nature of a marine biological adhesive on a low modulus, artificial surface. The visible response of the barnacle adhesive on silicone under external shear and tensile loading was suggestive of the viscous fingering seen in Saffman–Taylor instabilities. Complex branching separation occurred in rapid progression, usually within 100 ms. The results suggest that the barnacle adhesive exhibits rheological responses of a viscous material at the interface with silicone surfaces. Additional experiments with time-lapse photography demonstrated that the adhesive was stable underwater but became dehydrated or coalesced when exposed directly to air. A simple model of the adhesive system of a barnacle in contact with silicone based upon Balanus eburneus is proposed to assist in the development of a more complete understanding of barnacle adhesion.

Keywords: Barnacle adhesive; Fingering instabilities; PDMS silicone; Viscous separation

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INTRODUCTION

At present, there are no models available that accurately represent the mechanisms involved in barnacle adhesion and detachment from silicone fouling-release surfaces. In this study, an attempt was made to visually describe the characteristics and behavior of the adhesive of barnacles removed from silicones. For these experiments, the adhesive response to hand-applied forces in tension and shear was captured on high-speed video. Observations of the separation at the adhesive–silicone interface allowed for a phenomenological description of barnacle detachment. Based on the adhesive responses and observed viscous fingering during detachment of barnacles from silicone, we present a simple prototype for the development of a model for barnacle adhesion.

Barnacle adhesion is a topic of interest to scientists and engineers because of the impressive tenacity achieved by the adhesive and the capability of the bonds to form underwater. Mariners have long been aware of the barnacle's ability to attach to ships and the resulting detrimental effects on ship performance. Despite the use of antifouling coatings to prevent biofouling, barnacles continue to affect maritime activities. The United States Navy has a vested interest in understanding underwater biological adhesion and has supported a long-term research program aimed at the development of technology to achieve its prevention. For the past 12 years, research directed by the Office of Naval Research has been focused on development of coating systems that interfere with the attachment and adhesion of marine invertebrates through nontoxic means [1]. One promising technology has been the use of polydimethylsiloxane (PDMS) coatings. The chemical and mechanical properties of these materials reduce the normally tenacious attachment of barnacles to hard substrata (exceeding 1.0×10^6 N/m^2) to levels that enable easy removal (1.0×10^5 N/m^2) [2, 3].

Measurements of the force required to remove barnacles from experimental materials have routinely been performed with the use of a simple hand-held force gauge [4, 5]. The method provides an expedient way to determine the relative strength of attachment of barnacles to surfaces. These hand measurements taken on the same material on multiple occasions have shown repeatable results within a certain amount of variability [6–8]. The variability consists of biological, mechanical, and material factors (*e.g.*, organism growth and morphology, loading angle, and adherend composition and stability). Individual differences associated with the biology of the organism appear to contribute substantially to the variability in strength of

adhesion. This biological component of variability may derive from the genetic [9] or environmental history of the individual. Images presented here reflect the instantaneous response of adult barnacle adhesive in contact with silicone encountered by hand-applied loads.

The structure of the adult barnacle adhesive system must be known in order to understand its detachment. A schematic of the components of an adult balanid barnacle base is presented in a cross-sectional diagram in Figure 1 (adapted from reference 10). The structure may occur as one of several forms, but invariably there exists an interposed layer of secreted adhesive (also referred to in the literature as cement and plaque) between the shell and a surface. Inside the adhesive is a basement disc, the *basis*, consisting of a cuticular membrane, which may be wholly, partially, or not calcified [11, 12]. The acorn barnacles *Balanus eburneus* and *Balanus variegates*, which are characterized by calcareous bases and shells consisting of compartmental plates, were used in this study. The basis abuts or interlocks the peripheral shell plates at a basal suture where it grows incrementally with concentric additions [10–13]. Thus, the calcareous shell-wall plates are in contact with the substratum at the margin of the barnacle structure, and an adhesive covers the substratum within the circumference

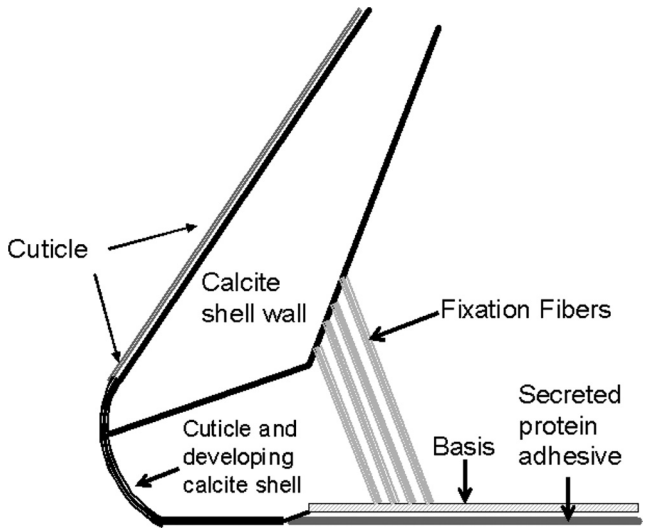

FIGURE 1 Cross-sectional diagram of the attachment and shell structure of a balanid barnacle (adapted from Bourget and Crisp [10]). Contact with the substratum occurs between the protein adhesive beneath the basis and the calcite shell at the margins of a circular or oval plane.

of the shell walls and beneath a membranous (in this case, calcified) basal disc.

Barnacle adhesive has been studied biochemically and structurally over several decades. It is known to consist mostly of protein in its pure form [14–17]. However, the conformations it may take while in contact with different substrata are not known although the adhesive has been shown to display variable bulk properties under certain conditions and when in contact with silicones [8, 18–22]. Images of three barnacles as viewed from the bottom through a glass panel coated with clear Dow Corning RTV 3140 silicone (Dow Corning, Midland, MI, USA) reveal the differences in the appearance of the bulk adhesive (Figure 2). One can generally say that the barnacle on the left (Figure 2a) is a form more readily seen under conditions of greater stability. In this form, the adhesive is transparent. This is also the morphology most often seen on uncoated glass. The radial pattern represents the internal calcareous structure of the barnacle basis, which is separated from the surface by the thickness of the adhesive. The barnacle in the middle (Figure 2b) represents a mixture of the transparent adhesive, around the margins where the basis structure can be seen, and opaque adhesive in the center, which obscures the basis infrastructure. The barnacle on the right (Figure 2c) is an example of totally opaque adhesive.

Barnacle adhesive begins as a clear, colorless liquid that is secreted through the basis from a network of glandular ducts [12, 18, 23].

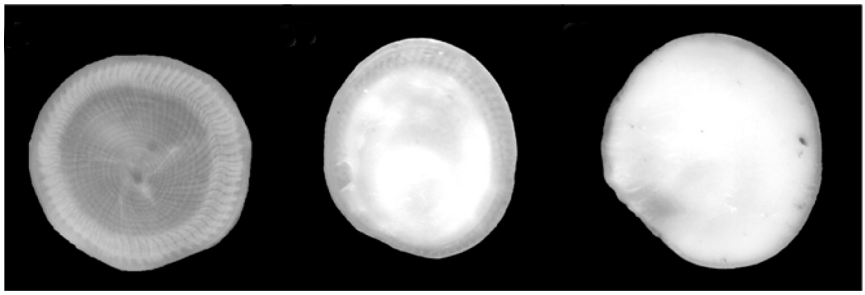

FIGURE 2 Photographs of bases of barnacles removed from Dow Corning RTV 3140 coating: a) barnacle with transparent adhesive; visible structures are of the basis infrastructure internal to the adhesive interfacial layer; b) barnacle with mixed adhesive properties; central opaque adhesive and surrounding transparent adhesive; and c) barnacle with opaque adhesive obscuring the basis.

Growth occurs with periodic, concentric radial increases, accompanied by adhesive secretions of proteinaceous cement to various portions of the basis [13, 14, 18, 19, 23, 24]. The protein then crosslinks to a polymer state with hydrophobic and disulfide bonds [25, 26]. The manner and degree to which crosslinking occurs on different substrata has not been defined, although differences in surface composition of the adhesive on synthetic polymers have been reported [22, 27]. How the differences in bulk adhesive properties affect the adhesion and debonding of the adhesive have yet to be fully described. However, the manner in which the adhesive material separates from a given substratum is dependent upon a dynamic interaction of the organism with the surface. The stability of the contact with the substratum is sensed by the organism through its connections with the shell walls, which are actively levered onto the surface, and through the transfer of forces between the surface and the adhesive. The production and composition of adhesives of different properties may be a physical or chemical response to various environmental interactions.

Characterization of the adhesive and its behavior during detachment from silicone may help determine the factors important in reducing the adhesion of marine invertebrates and allow for development of coating systems better able to resist biological deterioration of man-made materials in the sea. It is hoped that the qualitative description of the detachment of barnacles from silicones presented in this article prompts researchers with expertise in the fields of biology, adhesion, fracture mechanics, fluid dynamics, and rheology to investigate marine biological adhesive systems. Such research may eventually provide beneficial changes to our approach to producing environmentally sustainable antifouling marine coatings.

METHODS

Transparent PDMS coatings, represented by Dow Corning RTV 3140, T2 Silastic, and Sylgard 184, were applied to 100 $\times$ 200 $\times$ 4.76 mm glass panels at dry film thicknesses of 0.35 to 0.65 mm. The RTV 3140 elastomer is a one-part, moisture-cured PDMS, which forms hydroxyl-terminated polymer chains through reactions of acetoxysilanes. T2 Silastic and Sylgard 184 are platinum-catalyzed, two-component, hydrosilation-cured polymers with vinyl functional groups. The elastomers were allowed to cure in air for several weeks before testing. No solvent extraction was performed on the cured elastomer; however, the by-products of the elastomers used in this study are not known to be toxic. These coatings were exposed to barnacle fouling for several months in a natural estuarine environment, the Indian

River Lagoon, Florida, USA. When the barnacles reached sufficient size (5 to 15 mm in diameter), the panels were retrieved and cleaned of most biological material to isolate adult barnacles. The barnacles were maintained in aquaria for a short time until tested.

Barnacles were subjected to both shear and tensile forces. Two different methods were used to apply the shear forces. One method replicated the ASTM method [4] and applied the shear force manually to the base of the barnacle shell plate using a metal probe attached to a force gauge. The other method used clamps attached to two points of the shell, and applied shear loading to the clamps. Tensile forces were applied to barnacles by attaching clamps to the shell and manually exerting a normal force by hand. A Phantom v6.0 high-speed digital imaging system with a 55-mm lens (Vision Research, Inc., Stuart, FL, USA) was used to record the condition of the barnacle adhesive through the glass panel and transparent silicone (Figure 3). Images were acquired at rates ranging from 200 to 1,000 pictures per second. Recordings were analyzed for time-sequenced events, and representative frames were captured and are presented to visualize the debonding process during removal of the barnacle.

Long-term changes in the barnacle adhesive were examined by using a Nikon Coolpix 4500 digital camera attached to a Nikon SMZ-U dissecting scope (both from Nikon, Inc., Melville, NY, USA) to acquire time-lapse images at a frequency of one frame every 2 min. Barnacles were held in place, upside down, with plumber's putty for images of individuals removed from panels. For images of barnacles still attached to coatings, panels were placed upside down

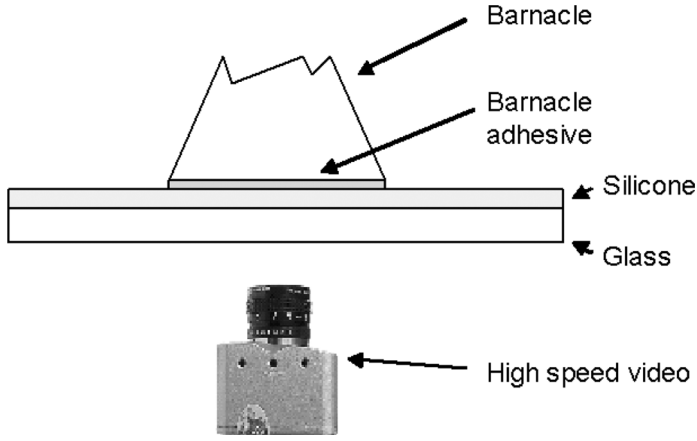

FIGURE 3 Data-acquisition design: high-speed camera and test panel.

over a glass dish containing seawater with just the openings of the tops of the barnacle shells protruding into the water. Instant Algae® microalgal concentrate (Reed mariculture, Inc., Campbell, CA, USA) was used to feed the barnacles during the experiments.

RESULTS AND DISCUSSION

Digital pictures acquired with high-speed video, usually representing a 1-ms interval, were analyzed and images selected to portray important events observed. Similarities were seen in adhesive separation of two species of barnacles from silicones with differing PDMS matrices. Variability in the adhesive structure, determined by visual opacity, was seen among and within individuals. The nature of the barnacle adhesive on silicones was further investigated with time-lapse photography to observe changes that occurred when exposed to air over time. From these observations, a simple model was developed to describe the adhesive components of a barnacle on silicone. The model is discussed in terms of viscous fingering phenomena known to occur in confined fluids.

HIGH-SPEED VIDEO OF BARNACLE DETACHMENT

High-speed video was acquired during the removal of a total of 40 individual barnacles from three silicone coating types. Each removal event was unique; however, the images obtained from these tests showed several common characteristics. These included a viscous adhesive interface with the silicone surface; initial separation, usually at the periphery of the basis; separation of portions of the adhesive prior to separation of the shell wall; a distinctive marginal shell-wall seal at the silicone contact; and both cohesive and adhesive failure of the barnacle adhesive. A detailed description of the detachment of *Balanus eburneus* in shear was made to discuss the components of the forced separation of barnacles from silicones. Results for tests in shear, in tension, and in shear surrounded by dye-colored water are also included to emphasize a range of responses possible for detachment. In the images, areas that appear with bright intensity are areas of barnacle-adhesive separation.

Shear Loading by Hand

An adult *Balanus eburneus* was isolated on a 0.35 mm thick RTV 3140 coating, and high-speed video was acquired during detachment in shear (Figure 4). The panel was air dried to remove water from the

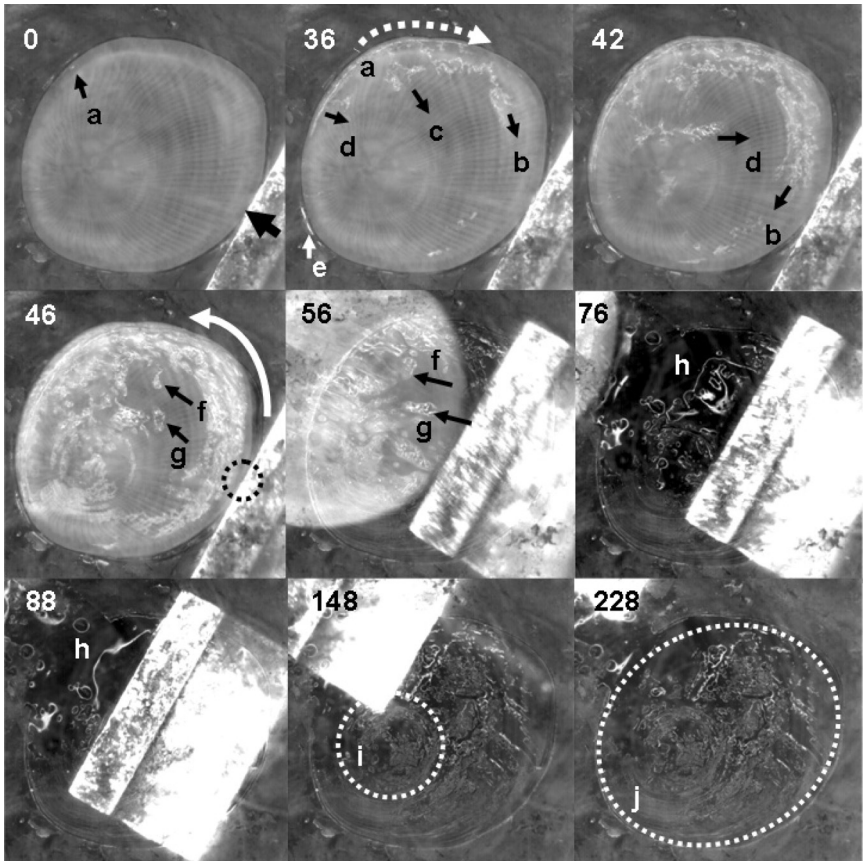

FIGURE 4 Adhesive separation under shear loading of a barnacle attached to Dow Corning (RTV) 3140 silicone (0.35 mm thick). Numbers in upper left corner of images represent time in milliseconds (ms). Testing was done in air. Probe direction: bottom right to top left. 0 ms: initial separation at (a). 36 ms: peripheral fingering instabilities at (b), (c), and (d) advancing toward the probe in direction of dashed arrow. Increasing pressure is reflected in the light intensity seen in the silicone outside the shell margin at (e). 42 ms: complex branching separation. 46 ms: viscous separation; see examples (f) and (g), with torsion (solid arrow). 56 ms: Progression of (f) and (g). 76 ms: viscous material at (h). 88 ms: viscous movement (h) in front of probe. 148 ms: remnant viscous reorganization in dashed circle at (i); see enlargement in Figure 6. 228 ms: solid remnant adhesive material at (j) and permanent deformation of the silicone at the marginal shell contact denoted by dashed oval (compare with previous image, 148 ms).

surface before testing. The duration of the captured video was 1 s at 1000 pictures per second (pps), and the majority of the separation and detachment of the barnacle occurred during a 30 ms time period. The time elapsed from the start of applied load until the initiation of the separation leading to detachment was 532 ms. During this first half-second (not shown), microscopic cavities were seen to appear at the periphery of the basis of the barnacle opposite of the point of applied load. At least four different points of separation appeared and grew slightly, then shrank, and either disappeared or relocated by distances of millimeters. Once catastrophic separation had begun, detachment of the barnacle occurred within a span of 76 ms. The sequence of events in Figure 4 starts at time = 0.

Adhesive Separation Phase

Separation proceeded from the initiation point (a) in Figure 4 (0 ms) circumferentially toward the applied load. At 36 ms, adhesive separation advanced *via* fingering instabilities away from point (a) and diverged in dichotomous branching at (b), (c), and (d) around the perimeter of the basal area. The instabilities grew into the center and became more complex peripherally as the pressure increased (42 ms). The increasing stress to the system can be noted by the change in reflective intensity in the silicone coating just outside the barnacle shell at point (e).

Detachment Phase

Adhesive separation progressed to an area representing one-half of the barnacle-adhesive contact by 46 ms; thereafter, the events reflected a detachment phase with complete debonding proceeding rapidly from this point onward. Total displacement of the barnacle from its original location by one basis diameter ($\sim$15 mm) occurred over a 30-ms span of time. Close examination revealed a counterclockwise rotation of the shell during the detachment (indicated by the solid white arrow, 46 ms). The viscous nature of the interfacial layer was seen throughout the images from 46 to 76 ms. Areas of adhesive appeared to move in distinct deformable pockets under the structure of the shell as the barnacle separated and moved over the surface. An example of this could be seen by following the points (f) and (g), denoted by arrows on the images of 46 and 56 ms.

Quantitative analysis of the displacement of the barnacle (see graph in Figure 5) was made using the point of contact of the probe face with the barnacle shell at 44 ms as the point of reference (dashed circle in Figure 4, 46 ms). Displacement over time was followed with

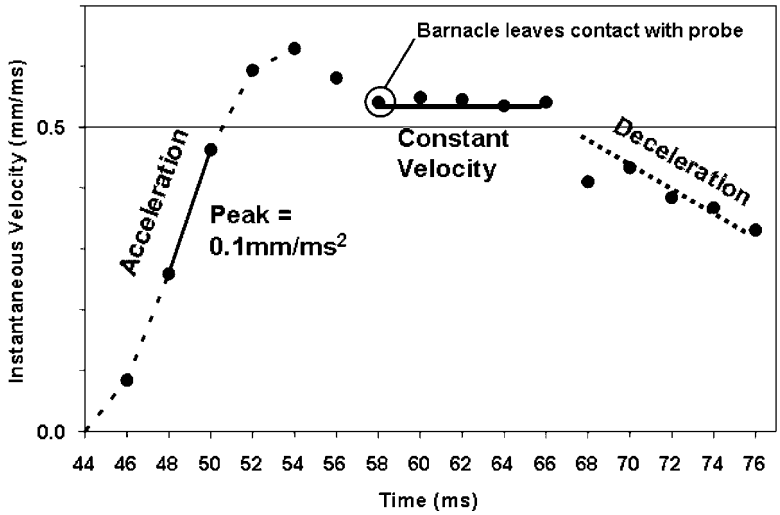

FIGURE 5 Instantaneous velocity (mm/ms) *versus* time (ms) of the detachment phase of the barnacle from Figure 4 under shear loading from 46 to 76 ms. Dashed circle (Figure 4, 46 ms) represents point of reference. Setting 44 ms as $t = 0$, we measured displacement from the point of contact of the shell edge and the probe face every 2 ms. Acceleration occurred for the first 10 ms, followed by slowing for 4 ms, until the barnacle lost contact with the probe, and continued sliding at constant speed for 8 ms, finally decelerating as a result if friction with the surface for the final 10 ms. Slope of the curve represents acceleration, with a peak of $\sim 0.1\,\mathrm{m/s^2}$ between 48 ms and 50 ms. The barnacle body traveled for 8 ms at a constant velocity equivalent to 0.55 m/s after departure from contact with the probe.

digital-image-analysis software, and the instantaneous velocity of the shell was calculated. The adhesive failure was characterized by shell acceleration between 44 ms to 56 ms, with a peak acceleration of $0.1\,\mathrm{m/s^2}$ (the slope of the line between 48 ms and 50 ms). This acceleration represents the release of the barnacle from a fixed position. The barnacle left contact with the probe at 58 ms, followed by 8 ms of constant velocity. At 66 ms, deceleration of the barnacle began and slowing because of frictional resistance continued until 76 ms, the time at which the barnacle was completely displaced from its original position. The 30-ms period of detachment of the barnacle, which produced a displacement of 15 mm, can be contrasted with the preceding 44 ms of adhesive separation, which was accompanied by a displacement of less than 500 μm.

Angular displacement (positive and negative) was observed during many, but not all, of the detachment events sampled. In two-thirds of the shear-loading samples, some rotation was seen. Of these, one-third showed minimal ($<5^{\circ}$) angular displacement. The others produced arcs that represented center angles of 5 to 30°. The motion relative to the initial position on the silicone was simultaneously forward shearing and rotational. This resulted from the geometry of the barnacle, application of loading, and adhesive characteristics. If the adhesive is anisotropic, then the stress field would be unequally distributed across the interface and torsion would be expected. In some cases, the rotation was induced by the shell-wall contact with the coating, as seen in Figure 4, 36 ms (e). Eccentricity, imperfect shear stress, and heterogeneity in the adhesive may all contribute to torsion. However, for barnacle detachment in shear the interaction of the perimeter shell with the silicone substratum can be another factor involved (the reason for this becomes apparent in the adhesive model section).

Reorganization Phase

Inspection of the area of coating previously in contact with the detached barnacle in the 140 milliseconds following its departure revealed a heterogeneous substratum consisting of a mixture of remnant solid, semisolid, and viscous fluid substance. The convoluted, bright-white pattern in the area between the probe and the departing barnacle, (h) at 76 ms, reflects viscous fluid material left behind on the silicone surface (darker area). The probe contacted the coating after recoil and slid across the surface, pushing the fluid material before it; see area (h) at 88 ms. After the probe had passed the area of interest, a remnant substance continued to move on the surface and reorganize in multiple directions; see area (i) demarcated by the dashed circle at 148 ms. To see this more clearly, images from 148 ms and 228 ms have been enlarged and enhanced (Figure 6). The material at (i) expanded and coalesced during the 80 ms observed. The area of concentric lines to the right of (j) at 228 ms corresponded to solid adhesive remaining on the silicone surface. This has been verified in previous research using protein stains [12, 28, 29].

The elliptic impression of the barnacle in Figure 4, 228 ms, overlain by the dashed oval (see 148 ms for comparison), reflects permanently deformed coating from the marginal contact with the barnacle shell. Such permanent coating deformation, a result of shell-plate growth, is commonly observed for low modulus coatings. All adhesive material can be removed by cleaning after the test; however, the depression in the coating from the shell margin remains.

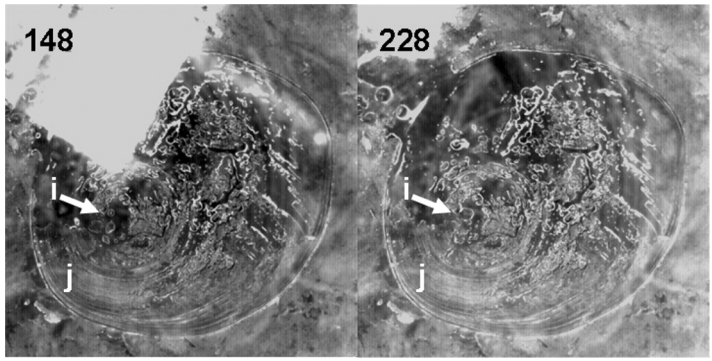

FIGURE 6 Adhesive mobility and reorganization after removal of the barnacle, enlargement of Figure 4 (148 ms and 228 ms). Features of the surface formerly in contact with the barnacle basis indicate cohesive failure of the barnacle adhesive. An area of fluid adhesive reorganization at the center of the basal contact shows several points (solid arrows) of roughly circular shape, which increase in size through spreading and coalesce into a larger feature. (j) Concentric rings indicate solid adhesive near the periphery of the basal contact.

Additional Shear-Loading Examples

Examples from two other hand-applied shear tests are included to show that similar responses were seen on other silicones and to emphasize the viscous response of the adhesive. Figure 7 shows the detachment of *Balanus variegates* from 0.65 mm thick T2 Silastic silicone, which was allowed to dry before testing. Force was steadily

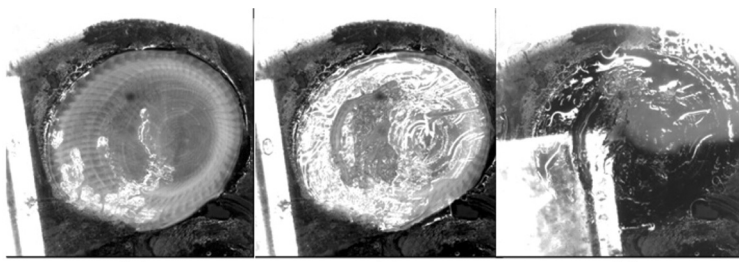

FIGURE 7 Adhesive separation under shear loading of *Balanus variegates* attached to Dow Corning T2 Silastic silicone (0.65 mm thick). Complex viscous fingering and cohesive failure of the barnacle adhesive is exhibited during detachment. Probe direction left to right.

increased for 645 ms before separation began. Once separation was initiated, fingering instabilities were seen to advance away from the probe rapidly (left to right in Figure 7a). The adhesive separation progressed to the majority of the basis area in 20 ms (Figure 7b). Detachment occurred over the following 70 ms, and left a residue of adhesive on the coating (Figure 7c).

Figure 8 presents results of *Balanus eburneus* on 0.6-mm RTV 3140 coating, tested before the panel was allowed to dry. Figure 8a shows the barnacle at the start of applied pressure. After 478 ms of steadily increasing load, the position of the barnacle can be seen to have been displaced by one-half base diameter without visible disturbance to the adhesive (Figure 8b). Sudden instability was generated at the periphery of the basis, point (a), and branching separation was seen to follow the curvature of the margin of the basis and grow inward toward the basis center (Figure 8c). The test concluded after 1 s with the barnacle completely displaced from its starting position on the panel but still attached to the coating.

Tensile Load by Hand

A tensile force was applied by hand to the barnacle by using clamps to secure the barnacle shell (Figure 9, 0–224 ms). The panel was dried to remove water from the coating surface. Images were captured with a 1-ms interval and 1-ms exposure. The adhesive separation initiated at a point inside of the peripheral shell wall in the vicinity of one of

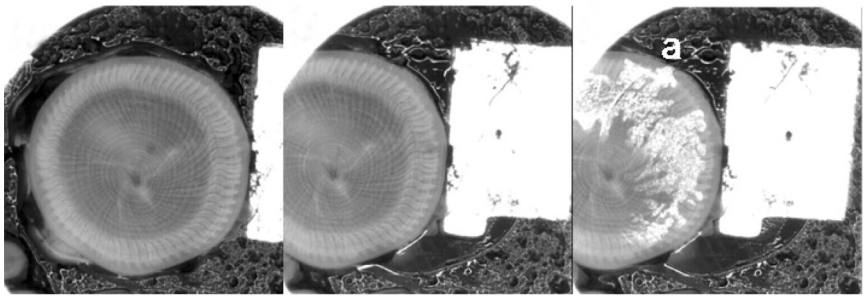

FIGURE 8 Adhesive separation under shear loading of *Balanus eburneus* attached to Dow Corning RTV 3140 silicone (0.60 mm thick). The panel surface was not dried before testing. The barnacle moved one-half base diameter before a visible response in the adhesive was seen. The barnacle was still attached to the coating at the end of the test. Probe direction right to left.

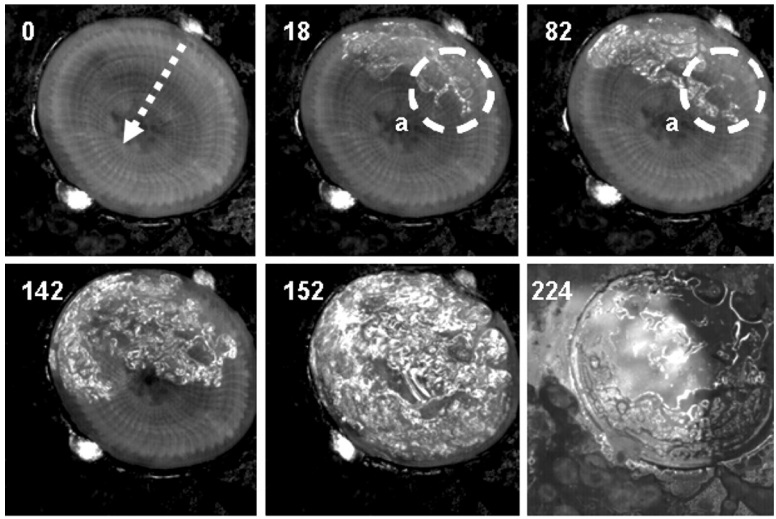

FIGURE 9 Adhesive separation under tensile loading of *Balanus eburneus* using clamps at two points of contact (bright objects at top right and bottom left of the barnacle image). Panel was air dried prior to testing. Numbers in upper left corner of images represent time in milliseconds (ms). Adhesive separation initiated at a point within the peripheral shell wall near one clamp at the top of the image, and progressed across the basis toward the other clamp (dashed arrow, 0 ms). Adhesive "healing" was seen after the separation front had passed some areas [see dashed circle, (a) at 18 ms and 82 ms]. Separation progressed to a complex pattern across the entire basal interface until detachment occurred at 224 ms, leaving remnant adhesive on the surface.

the clamps and progressed generally from one side of the basis to the other (dashed arrow in Figure 9, 0 ms). Detailed examination revealed separation (~150 ms for detachment) by fingering propagated in several directions simultaneously. Adhesive "healing" was observed (Figure 9, compare [a] at 18 ms and 82 ms) for some areas after passing of the separation front. The separation progressed from half the adhesive area to full detachment (Figure 9, 142–152 ms) in a very short interval of time (~10 ms). Detachment occurred as cohesive failure of the barnacle adhesive (Figure 9, 224 ms).

Ink Tests

The previously presented observations were performed in air; however, the natural medium for a barnacle is water. High-speed videos of barnacle-adhesive separation patterns underwater were difficult

to visualize because of the ingress of water, removing the contrast that was created between the viscous interface and air. To enable visualization of underwater detachment, the water was colored by ink. The method was implemented by constructing a retaining wall sealed with silicone on the coating surrounding the barnacle. The space between the attached barnacle and the wall was filled, as a moat, with water colored with ink.

Ink Shear Test

This test was performed by hand-applied force on 0.5 mm thick Dow Corning Sylgard 184 coating with a 5-ms interval and 1-ms exposure (200 pps). Barnacle removal was recorded over a period of 1 s. Clamps were attached at two points [(a) and (b) in Figure 10, 0 ms], and a shear load was applied along the longitudinal axis (solid arrow in Figure 10, 0 ms). Separation occurred within the adhesive at a point in proximity to, but separate from, the outer shell wall [dashed circle, area(c) in Figure 10, 0 ms]. The circumferential shell wall appeared to stain from absorption or seepage of the surrounding ink (darkened peripheral ring denoted by dashed arrows in Figure 10, 0 ms). The separation proceeded as a nonuniform wave toward the center of the basal area (Figures 10, 0–450 ms, solid black arrows showing direction of movement) until more than half of the adhesive had separated. This separation appeared to be a gas-filled cavity, which remained stationary as other changes occurred, until final detachment.

At 510 ms [Figure 10, point (d)], the outer seal of the shell-wall contact was broken and ink intruded into the barnacle area of separation. The ink entered the area under the barnacle and filled the void created by the original separation. The advancing ink was seen to reverse direction briefly, [point (e) in Figure 10, 705 ms and 810 ms], then proceed along the path previously occupied. This reversible advancing and receding occurred twice and coincided with the development of other separations, e.g., the second break in the outer shell seal at (f) in Figure 10, 705 ms. The two intrusions of ink joined in Figure 10, 900 ms, where upon the progression of the ink and complete barnacle detachment occurred rapidly. The time elapsed from Figure 10, 900 ms, to complete detachment was 70 ms. After removal of the barnacle, small bubbles, presumably gas, were seen [point (g), circled in Figure 10, 970 ms] lingering briefly (30 ms) on the coating surface within the previously occupied area of contact of the barnacle adhesive.

Ink-Tensile Test

Results of a second ink test are presented to show the extent to which fingering occurred during intrusion by the dye-colored water

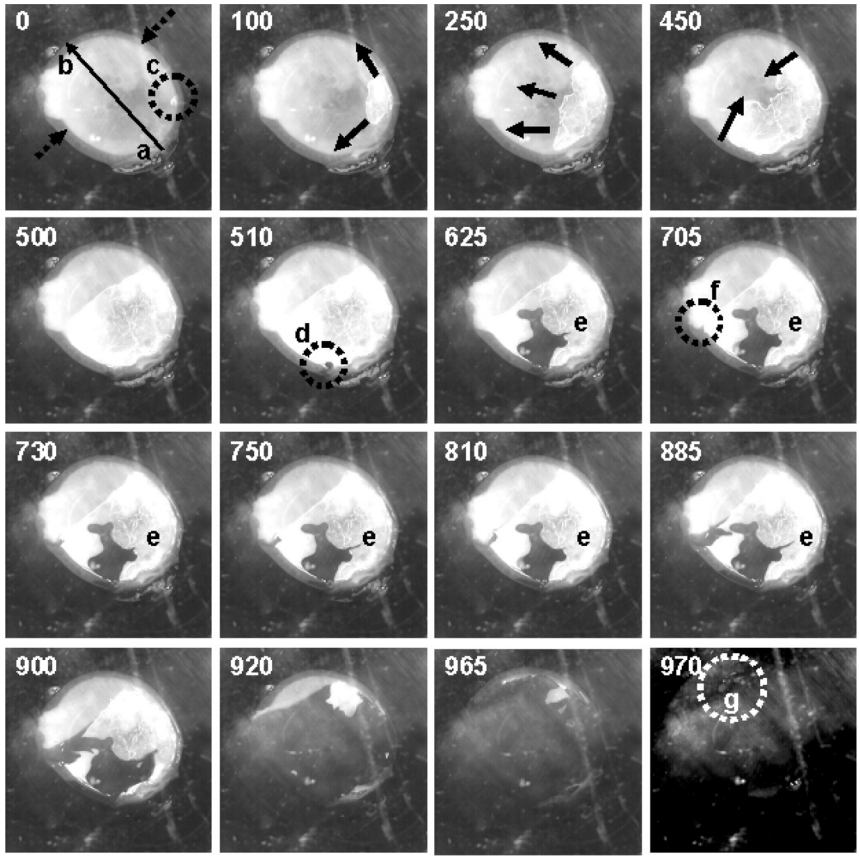

FIGURE 10 Ink shear test (applied with clamps) of a barnacle attached to Dow Corning Sylgard 184 silicone (0.5 mm thick). Numbers in upper left corner of images represent time in milliseconds (ms). 0 ms: separation initiation (c) at periphery of the basis, solid arrow (a) to (b) shows direction of applied force, dashed arrows indicate staining from the dye around the margin of the basis. 100–450 ms: solid arrows indicate direction of separation growth. 510 ms: seal at the shell margin breaks (d), ink intrudes. 625 ms: fingering progression of ink. 705 ms: receding ink finger at (e), simultaneous break in shell seal at (f). 730–885 ms: continued progression of ink fingers at (e) with a second retreat of ink along established path. 900 ms: ink joins. 920 ms: detachment of the barnacle proceeds rapidly. 965 ms: barnacle detached. 970 ms: remnant bubbles dashed circle at (g), presumably gas, disappeared from surface of silicone within 30 ms.

(Figure 11). Adhesive separation prior to the ink intrusion was not seen. This may have been due to the basis being cracked during removal. The advancement of the ink was characterized by limited fingering. The image sequence begins at 424 ms, and progresses until 1.58 s (Figure 11f), 10 ms before complete detachment.

TIME-LAPSE PHOTOGRAPHY

The adhesive of the barnacle is secreted through a basement membrane in a layer between the substratum and the barnacle shell housing, and within the periphery of the outer shell contact. The morphology of the adhesive has been seen to be quite variable on silicone substrata with visible characteristics ranging from transparent to opaque layers. A full description of the properties of the adhesive are beyond the scope of this article, (qualitative and quantitative descriptions have been made elsewhere [8, 13, 18, 20–23, 28, 29]; however, some time-lapse experiments were performed that assist in understanding the nature of this protein adhesive.

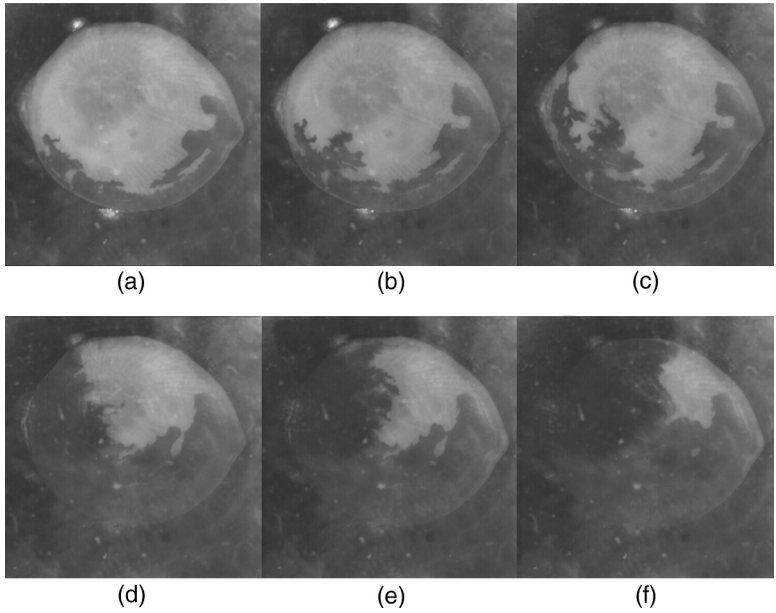

FIGURE 11 Ink tensile test (applied with clamps) of a barnacle attached to Dow Corning Sylgard 184 silicone (0.5 mm thick). Separation in the adhesive was not seen prior to intrusion of the ink. Fingering progression of the ink was less complex, and fingers appeared broader, than separation in air.

Time-Lapse Experiment 1

A barnacle was removed from the surface of a silicone coating, placed upside down in a bowl of sea water, and monitored over time with a digital camera acquiring single images every 2 min for a period of 24 h. As seen in Figure 12, no change in the adhesive layer of the barnacle was noted. The same, living barnacle was then removed and left in air, and single images were acquired every 2 min. After 4 h of exposure, the opaque protein consolidated. The infrastructure of the calcareous basis became visible, and white remnant adhesive was seen along fractures within the basis and at the resulting concave center of the barnacle. This concavity of the basis of some barnacle individuals was noted in Darwin's original descriptions [13] and has been reported by other researchers [18, 22], and appears to be related to the stability of the attachment by the adult barnacle. The degree of deformity of the bases directly relates to the volume and thickness of the adhesive, and perhaps its bulk properties. Personal observations of numerous (thousands) *Balanus eburneus* and *Balanus variegatus* individuals suggest that the adhesive layer present on smooth surfaces with firm attachment can be thin and consistent with little apparent deformation of the basis, for example uncoated glass or thin films (<100μm) of silicone. Lindner [19] suggested a thickness of 5 μm for such adhesives, whereas as Soroyan *et al*. [18] suggested 50 μm, although how such measurements were derived was not stated. Under such conditions, the adhesive is added in distinct circumferential bands, as shown in Figure 13, and previously described by Walker [12]. Under conditions

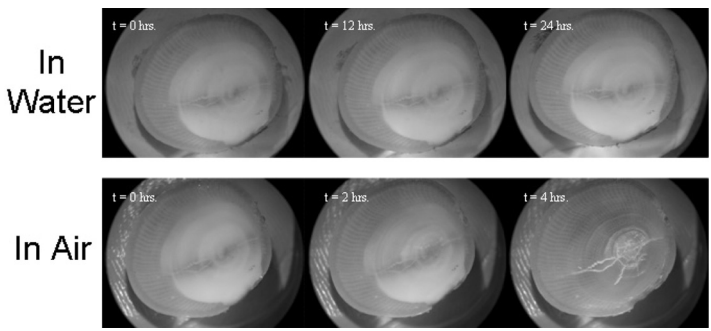

FIGURE 12 Changes in basis of barnacle removed from silicone coating, partially composed of opaque adhesive: (top) in water for 24 h showing no change in properties and (bottom) the same barnacle in air 4 h after removal from water. The opaque adhesive appears to dehydrate and consolidates along the cracks and in the center of the basis.

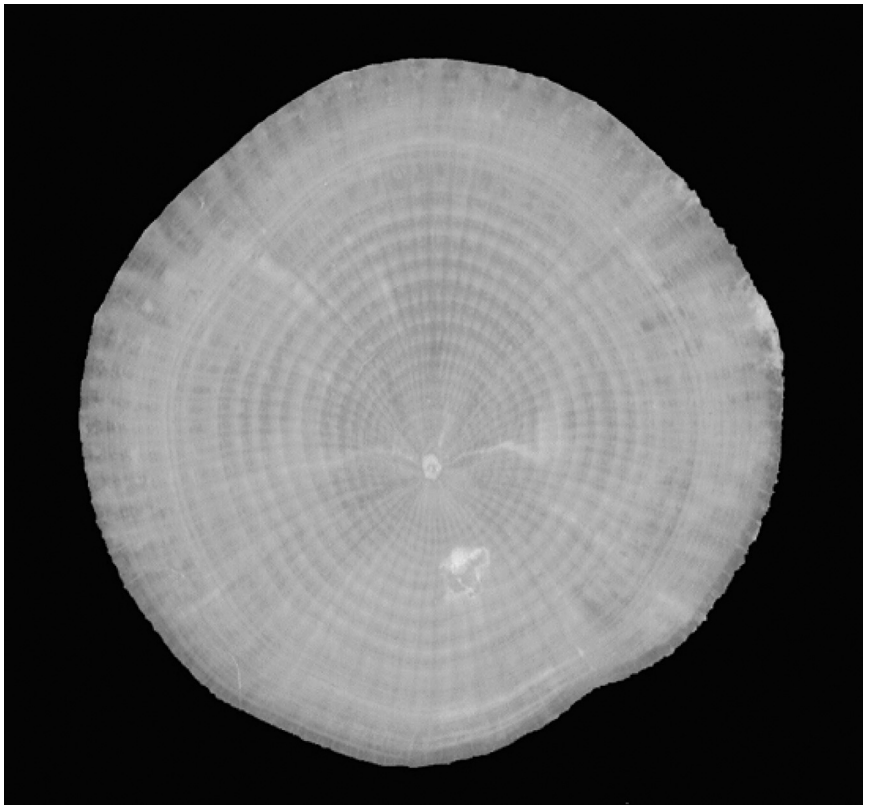

FIGURE 13 Barnacle viewed from the bottom adhered to glass showing radial growth pattern of the calcite basis and the concentric rings of adhesive additions.

of instability, greater volumes of adhesive are produced between the basis and the substratum [21]. This is supported by personal observations, which have shown thickness for opaque adhesive formation to range up to millimeters. The morphology of the adhesive has been observed to change, and the composition or conformation of the protein adhesive in such circumstances may also change.

Time-Lapse Experiment 2

Additional time-lapse tests were made looking for changes occurring with the barnacle still attached to the coating. A barnacle was monitored with the digital camera as before, focused on the basis through the glass panel and clear silicone coating. The barnacle was suspended

over a bowl of sea water, such that the opening of the shell projected into the sea water and the barnacle was able to feed and survive for an extended period of time. After 9 days, no change was seen on the basis of the barnacle. The sea water was then removed and the monitoring continued. After 15.5 h the barnacle was seen to detach from the panel under force of gravity, aided in part by the movement of the barnacle within the shell.

It should be noted that the type of adhesive failure described is not characteristic of the adhesive in contact with other artificial substrata such as aluminum, glass, or epoxy, or natural substrata, such as rock or wood, where the attachment of the shell remains strong long after exposure to air and beyond the death of the barnacle. Attachment under such conditions may be envisaged as an interaction between a stable substratum and a thin, highly cross-linked protein polymer with unknown interfacial characteristics.

Examination of a silicone surface after detachment of adult barnacles sometimes reveals depressions in the coating matching the outline of the shell margin of the barnacle contact area. Visual evidence of this effect has been noted in testing of polymeric coating materials. Disintegration of protective coatings by the penetration of the shell wall through growth has long been known [30]. Silicone coatings are often physically breached and undercut by the downward force and outward growth of the barnacle shell. In many cases, the silicone is not entirely cut; rather, it is permanently deformed in a circular ring matching the area of contact of barnacle shell plates with the coating surface. This coating deformation is achieved by pressure exerted through the attachments of muscle and ligament from the barnacle to the internal surface of the basis and the internal wall of the shell plates, which have been described by several authors [10, 12, 13]. Silicone panels that have been deformed by adult barnacles, and subsequently stored in laboratory conditions, have retained these deformations for years (see Figure 14).

ADHESIVE MODULUS

The qualitative descriptions that were permitted by the time-lapse experiments of the variable properties of the adhesive focus on the bulk of the material, but it is the interface that is of interest in this study. Recent investigation with atomic force microscopy [29] of the surface properties of the barnacle adhesive detached from silicone surfaces revealed a layered, low modulus (10^5 Pascal), heterogeneous material with successively increasing moduli from the contact surface toward the basis. The modulus of the peripheral shell displayed a

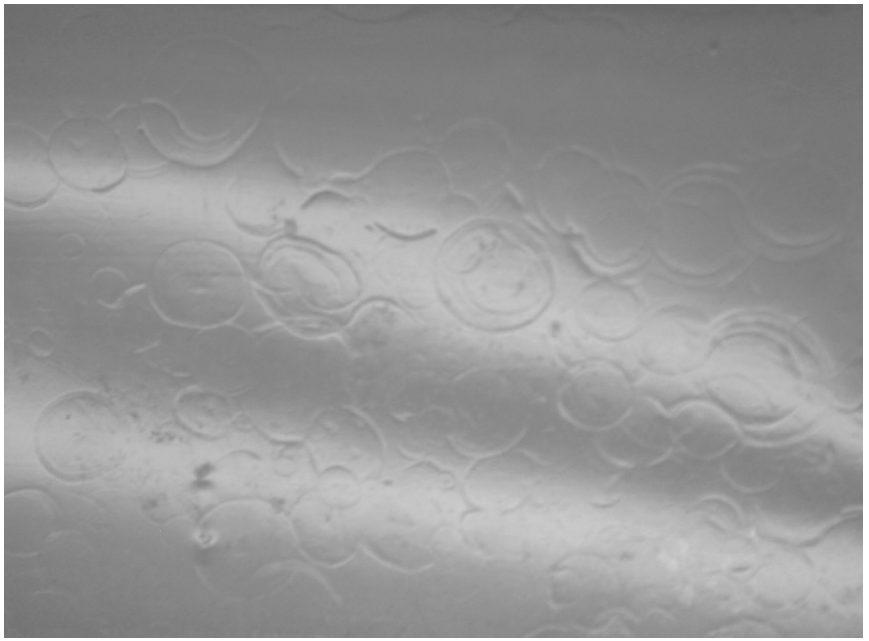

FIGURE 14 Surface of a silicone coating showing impressions produced by the growth of barnacles persistent after 3 years of storage in laboratory conditions. (See COLOR PLATE II)

much higher value (10^9 Pascal). Measurements with an atomic force microscope interrogated the surface to a depth of 300 nm of the adhesive. The video imaging of separation obtained for the present study suggests that the low modulus solid adhesive is separated at the interface from the silicone substratum by a viscous material of unknown composition. From previous work described in the literature combined with insights from this study, we constructed the following conceptual model of balanid barnacle structural attachment to silicone. The model, based upon *Balanus eburneus*, is presented as a foundation upon which a more elaborate description might be derived as our knowledge of the nature of barnacle adhesive increases.

BARNACLE–SILICONE ADHESION MODEL

A hypothetical *Balanus eburneus*–type adhesive system, in contact with silicone, consists of a circumferential seal at the bottom edge of the shell enclosing a heterogeneous, low modulus solid to semisolid protein adhesive with underlying colloidal interfacial material that

displays viscous properties (Figure 15). The interaction of the shell with the silicone reflects one level of adhesion consisting of forces of contact between calcite and methyl siloxane, and, in some cases, an increased mechanical resistance to shear through deformation of the silicone substratum. A gradient of adhesive modulus (from relatively high to low) describes the adhesive transition from the adhering organism basement membrane to the substratum. This may be achieved through variable cross-linking or variation in the composition of the protein. Such a gradient may occur through increased water content with distance from the basal membrane as speculated by Wiegemann [22] based on histological staining and scanning electron microscopy images of barnacles removed from a commercial silicone. This proposal has some quantitative support in the findings of Fant *et al*. [31], who described increased water content of marine mussel protein adsorbed to methylated surfaces compared with silicon surfaces, using quartz-crystal microbalance techniques with synthetic Mefp-1 byssus thread protein. A reduced modulus would change the adhesive capability of the barnacle with an exaggerated viscoelastic effect. A colloidal interface allows for the observed lateral displacement of the body through viscous flow, without loss of surface contact.

Viscous Fingering Phenomena

The interfacial adhesive layer of the barnacle confined within this perimeter seal and adhered to a silicone substratum has been shown to respond to externally applied shear forces with viscous fingering.

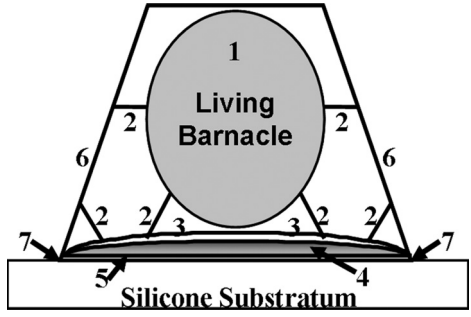

FIGURE 15 Conceptual illustration of barnacle attachment to silicone consisting of 1) living soft-bodied barnacle; 2) muscle and tendon attachments between the body, the shell plates, and basis; 3) membranous basis, calcified or uncalcified; 4) solid to semisolid protein adhesive; 5) viscous adhesive interface; 6) calcite shell walls; 7) and shell seal with silicone substratum.

The phenomenon of viscous instability of a lower viscosity fluid penetrating a higher viscosity fluid was described by Saffman and Taylor [32] using the Hele-Shaw cell [33]. Extensive research of the phenomenon of induced patterns of flow has produced a general understanding of separation of confined fluid substances [34–42]. The phenomenon of fingering instability has been extended to materials beyond liquids, and may be applied to non-Newtonian fluids, for example, clay slurries [43]. Fingering instabilities have also recently been observed in confined solid films [44–47]; however, this type of instability has been attributed to elastic deformation processes. Whereas the Saffman–Taylor problem involved the simplest case of pure Newtonian fluids between parallel plates, the case at hand is likely to involve a complex fluid interaction resulting in more diverse fingertip splitting as seen in studies of non-Newtonian fluids [48–50]. Furthermore, the boundaries consist of one smooth, potentially flexible surface (silicone) and another concave, reinforced polymer disc (basis membrane). The intervening protein fluid exhibits a remarkable range of material states, which may allow for a variety of separation outcomes. It is, therefore, suggested that the adhesive exists as a gradient from a solid viscoelastic polymer nearer the barnacle basis to a viscous gel at a silicone surface. The ratio of adhesive material phases and their control have yet to be worked out; however, predominance of one or another phase could lead alternately to viscous fingering in the case of colloidal gel and fracturing for more viscoelastic states. This is dependent on the ratio of internal relaxation time to the time scale of a flow event (see Lemaire *et al*. for full discussion) [51].

CONCLUDING REMARKS

If the barnacle adhesive in contact with silicone substrata is viewed as a viscoelastic gel, adhesion will contain a viscosity term and become a problem of tack. This was intuitively suggested by Crisp [52] when he proposed Stefan's adhesion [53] as a possible mechanism for adult barnacle adhesion. His suggestion was presumably based upon observations of barnacles adhered to glass moved by a distance of centimeters over several months' time without becoming detached and while continuing to grow in size [54]. The displacement was caused by the lateral forces exerted by other more strongly adhered barnacles as they grew. Crisp and Walker [55–57] later revisited this topic because Stefan's description considered only Newtonian fluids under tensile loading.

A number of unique observations relating to the detachment of barnacles from silicone surfaces have been made with the use of a

high-speed digital camera. Forty separate tests using a handheld probe to apply both shear and tensile forces to two different species of barnacles collected repeatable data from three PDMS silicone coatings. The data indicated that the interfacial layer that separates the barnacle from the silicone has viscous properties. Separations were initiated within the adhesive at the periphery of the basis and progressed through complex multidirectional fingering to a point (usually after half of the area had separated) when the outer seal of the shell wall failed. Complete detachment rapidly followed. The detachment sequences induced by hand-generated forces generally occurred within 100 ms from initial separation to removal. Shear and tensile loads produced similar modes of failure. Underwater tests, with ink dye, revealed a similar succession of adhesive failure, but with much less fingering during separation progression.

This study provided qualitative indications of viscous adhesive properties and generates questions that may be answered through quantitative testing of simultaneous force and displacement measurements with visual acquisition of detachment. The results assist in the development of a model, counter to a purely elastic view, of barnacle adhesion to silicones. In a broader view, barnacle adhesive appears to be variable and dynamic, displaying differences in properties in response to differences in stability of substrata. The measurement of adhesive properties collected from barnacles with differing interfacial interactions will be needed for a fuller understanding of barnacle adhesion.

Antifouling polymer coatings research has progressed to a point where experts from several fields of study, namely adhesion and fracture mechanics, can significantly advance our understanding of the fundamental aspects of biological adhesion. This may contribute to the development of new, sustainable, and environmentally sound technologies to protect man-made structures from biofouling. By understanding the adhesion mechanisms of organisms to substrata and how that mechanism can be disrupted, we may enable the replacement of current practices of using biocide-based paints in the marine environment.

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