Factors that influence elastomeric coating performance: the effect of coating thickness on basal plate morphology, growth and critical removal stress of the barnacle *Balanus amphitrite*

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Abstract
Silicone coatings are currently the most effective non-toxic fouling release surfaces. Understanding the mechanisms that contribute to the performance of silicone coatings is necessary to further improve their design. The objective of this study was to examine the effect of coating thickness on basal plate morphology, growth, and critical removal stress of the barnacle *Balanus amphitrite*. Barnacles were grown on silicone coatings of three thicknesses (0.2, 0.5 and 2 mm). Atypical (“cupped”) basal plate morphology was observed on all surfaces, although there was no relationship between coating thickness and i) the proportion of individuals with the atypical morphology, or ii) the growth rate of individuals. Critical removal stress was inversely proportional to coating thickness. Furthermore, individuals with atypical basal plate morphology had a significantly lower critical removal stress than individuals with the typical (“flat”) morphology. The data demonstrate that coating thickness is a fundamental factor governing removal of barnacles from silicone coatings.

Introduction
There has been considerable effort over the past 25 years to develop non-toxic, foul-release coatings to aid in the control and prevention of biofouling (Swain, 2004). This effort has been driven mainly by environmental regulations that have reduced or in some cases eliminated the use of highly effective toxic paints (e.g. triorganotin-based paints) (Walker, 1998). In contrast to toxic paints, which prevent the recruitment and growth of organisms on surfaces, non-toxic coatings allow biofouling to occur and instead rely on the inability of organisms to adhere well to surfaces. Weak adhesion by organisms facilitates their removal through factors such as biotic disturbance or hydrodynamic forces (e.g. Swain et al. 1998; Schultz et al. 1999).

The most effective non-toxic surfaces to date are silicone-based elastomeric coatings. Much of the knowledge of best performing coatings has been derived empirically through extensive laboratory and field testing of emerging coatings (e.g. Swain et al. 1992; Swain & Schultz, 1996). However, current understanding of the mechanisms by which elastomeric coatings provide easy release is at best incomplete. It has been demonstrated that a variety of factors influences the performance of elastomeric coatings. For example, silicone fluids or the incorporation of oils enhance the performance of elastomeric coatings (e.g. Truby et al. 2000; Kavanagh et al. 2001; 2003; Stein et al. 2003). It is also known that certain factors are important such as surface energy (e.g. Baier et al. 1968; Finlay et al. 2002), coating modulus (e.g. Brady & Singer, 2000; Singer et al. 2000; Berglin et al. 2003; Chaudhury et al. 2004), frictional slippage (Newby et al. 1995; Newby & Chaudhury, 1997), and coating thickness (Kohl & Singer, 1999; Brady & Singer, 2000). However, the practical importance of the aforementioned factors has not been thoroughly examined in situ using live organisms. It is thus not clear whether such factors are applicable to the release of hard-fouling from elastomeric coatings under natural conditions. The primary objective of this study was to examine using live barnacles the effect of coating thickness on the performance of elastomeric coatings.
The notion that coating thickness is important to performance is based on a fracture mechanics model developed by Kendall (1971). Kendall showed that the force required to pull off a rigid cylinder attached to a thick elastomer is given by

\[ P_c = \pi a^2 \left( \frac{8Ew_a}{\pi a (1 - v^2)} \right)^{1/2} \quad (1) \]

where \( P_c \), \( E \), \( w_a \), and \( a \) are crack initiation force, elastic modulus, Dupre’s work of adhesion between epoxy and elastomer and contact radius, respectively. However, if the contact radius is much larger than the elastomer thickness, i.e. \( a \gg h \), where \( h \) is the thickness of the elastomer, then the crack initiation force is given by

\[ P_c = \pi a^2 \left( \frac{2w_a K}{h} \right)^{1/2} \quad (2) \]

where \( K \), the bulk modulus of the elastomeric film is related to the elastic modulus by

\[ K = -\frac{E}{3(1 - 2v)} \quad (3) \]

Since \( K \gg E \), because \( v \) approaches 0.5 for an elastomer, a thin coating has a higher \( P_c \) than a more compliant thick coating.

Indeed, pull-off tests of epoxy bonded to silicone coatings (often called pseudobarnacle tests) have verified the behavior predicted by Kendall’s model (Kohl & Singer, 1999; Brady & Singer, 2000; Singer et al. 2000). However, the only two published reports to date using live animals (in contrast to pseudobarnacles) failed to find an inverse relationship between coating thickness and pull-off force (Singer et al. 2000; Sun et al. 2004). The absence of a thickness dependence found by Singer et al. (2000) was likely to be due to the fact that most of the barnacle basal plates broke during removal. In this case the mechanics of detachment should not follow Kendall’s model, which describes a fracture process where a basal plate would peel from an elastomer.

A proportion of animals growing on silicone coatings have been shown to have atypical basal plate morphology (sometimes referred to as “cupped”) that consists of a thick callosus of cement present between the calcareous basal plate and the substrate; the basal plate often forms a cup over this thick callosus (Watermann et al. 1997; Berglin & Gatenholm, 2003; Wiegemann & Watermann, 2003). Moreover, Holm et al. (2005) have shown that the occurrence of the atypical basal plate morphology has both an environmental and a genetic underpinning and that there is a significant interaction between these factors. Sun et al. (2004) suggest that atypical basal plate morphology may form as a result of increased production of adhesive as animals try to maintain contact with a PDMS substratum. In the present study tests were carried out to see if the atypical morphology may be in part related to the effective compliance of the substratum, and therefore, it was predicted that the frequency of the atypical morphology may increase on the thicker, more compliant coatings.

An initial study was conducted to determine which of two commercially available silicones, Sylgard 184™ or a cross-linked polydimethylsiloxane elastomer by Gelest™, hereafter referred to as PDMSdp125, gave the more effective foul-release surface. After determining that the PDMSdp125 was the more effective of the two, the earlier work with pseudobarnacles was then extended by using live barnacles on PDMSdp125 to investigate the effect of coating thickness on i) the rate of growth and size of individuals, ii) the frequency of atypical basal plate and adult cement morphology, and iii) critical release stress (sometimes referred to as adhesion strength). Attempts were also made to determine whether the critical removal stress differed between animals with typical (“flat”) and atypical (“cupped”) basal plate and adult cement morphology.

**Methods**

**Silicone materials**

Sylgard 184™ (Dow Corning Corp.) is a two-component, high-temperature-vulcanized (HTV) silicone elastomer. Following the product instructions, the base resin and curing agent provided in two separate containers were thoroughly mixed in a ratio of 10:1 by weight and cured at 85 °C for 2 h. The PDMSdp125 coatings were prepared from a base resin (vinylidimethylsiloxy-terminated polydimethylsiloxane, Gelest™ catalog DMS-V22, 200 cSt, 9400 g mole\(^{-1}\)(125 dp), 0.4–0.6 wt% vinyl) using a crosslinker (25–30% methylhydroxiloxane-dimethylsiloxane copolymer, Gelest™ catalog HMS-301, 25–35 cSt), a catalyst (platinum-divinyltetramethyldisiloxane complex, Gelest™ catalog SIP6830.0, 3–3.5% platinum concentration in vinyl terminated polydimethylsiloxane) and a curing control agent (Maleate, from Dow Corning). The mixture was cured at 75 °C for 1 h.

**Coating preparation**

Two sets of coatings were prepared at NRL for barnacle adhesion and removal studies. The first set was 10 slides each with 1 mm thick coatings of Sylgard 184™ and of PDMSdp125. The second set was PDMSdp125 coatings at thicknesses of 0.1 mm, 0.5 mm and 2 mm. To achieve the correct thickness, the silicone mixtures were poured into a cast
consisting of a microscope glass slide at the base and spacers on four sides of fixed height. The surface of the glass slide was coated with a silane coupling agent to promote bonding to the coating. After pouring the mixture, it was carefully covered by a hydrophobic glass slide to constrain the thickness of the mixture during curing; then the cast assembly was secured with six clamps. The assembly was placed in an oven where the mixture cured. After curing, the hydrophobic glass slide was removed. It should be noted that the process of using a hydrophobic glass slide can affect the surface properties of a cross-linked PDMS, and can differ from an air cured PDMS. The coatings were air-cured for several weeks before leaching. Measurements via indentation showed that the cured coatings acted as true elastomeric surfaces, indicating complete curing.

Ten slides of each thickness were sent to Cal Poly for barnacle studies and two slides remained at NRL for pseudobarnacle testing (to be reported in a separate paper). Both sets of coatings were leached in 0.2 μm filtered natural sea water for 6 d.

**Larval settlement and growth conditions**

*Balanus amphitrite* cypris larvae were obtained from the Duke University Marine Laboratory. A 500 μl drop of seawater containing 20 – 50 cypris larvae was placed on each treated microscope slide in a covered Petri dish. Cypris larvae were allowed to settle in these conditions for 72 h at 25°C in a constant temperature incubator under a 12 h light/dark cycle. After that time, each slide was transferred to a separate 100 mm × 20 mm Petri dish and immersed in 40 ml of natural, 0.2 μm filtered seawater. For the pilot study on two different commercially available PDMS formulations, settlement was performed on 28 April 2003. For the coating thickness experiment this was done on two separate occasions: 27 December 2003 and 27 February 2004.

Newly metamorphosed barnacles were fed the unicellular alga *Dunaliella tertiolecta* and the diatom *Skeletonema costatum*. Nauplius larvae of the brine shrimp, *Artemia sp.*, were added to their diet 2 weeks following settlement. Feeding was done every Monday, Wednesday and Friday, and involved a complete replacement of the seawater and food suspension within each Petri dish. Animals were reared at 25°C in a constant temperature incubator under a 12 h light/dark cycle.

**Growth of basal plate**

Barnacles growing on 5 slides of each thickness were monitored monthly from 31 December 2003 to 31 March 2004 to determine if there were any differences in growth rate of the basal plates as a function of coating thickness. Photography was performed using a Canon™ EOS 10D digital camera attached to an Olympus™ SZX12 dissecting microscope. The basal plates of the developing barnacles were photographed through the transparent substratum, and the area of the basal plate was calculated using NIH’s ImageJ image analysis software. Basal plate areas were compared by analysing data from 31 March 2005 in one- and two-factor ANOVAs.

**Shear testing**

The shear test apparatus consisted of an IMADA™ AXT 70 digital force gauge (2 kg) mounted on an IMADA™ SV-5 motorised stand. The force gauge was attached to a motorised stand that moved a shearing head parallel to the coating surface at an average speed of approximately 67 μm s⁻¹. The glass slides were clamped into a custom-built Plexiglas chamber that allowed complete submersion of coatings during release tests. Prior to each test, basal plates were photographed using a Canon™ EOS 10D digital camera attached to an Olympus™ SZX12 dissecting microscope, and areas were calculated using NIH’s ImageJ. As the coating surface was flat, barnacle adhesive was assumed to be in contact with the substratum over the entire basal plate surface; therefore the size of the basal plate was measured to determine area. Only barnacles with a diameter >3 mm were shear tested. The force at which the barnacle detached from the coating, the maximum force measured, is hereafter called the critical removal force; the critical removal stress is obtained by dividing the critical removal force by the measured basal area. The shear test was discarded in cases where any fraction of the basal plate remained attached to the surface. Procedures for performing shear tests differed from ASTM D 5618 in that the shear force was applied by an automated test stand and the barnacle release was performed in water. In June 2003, shear tests were performed on the first set of PDMSdp125 and Sylgard 184™ (1 mm thick) coatings. The second set (0.2, 0.5 and 2 mm thick) of coatings was shear tested on two occasions: mid-February and mid-June 2004. Data from shear testing satisfied the assumptions for an ANOVA, and were analysed using one-and two-factor ANOVAs and Fisher’s PLSD post-hoc tests.

Photographs were also used to determine the morphology of the barnacle basal plates. The atypical or altered cement produced by barnacles growing on silicone surfaces could be observed visually as a white mass that obscured the radial structures characteristic of the barnacle’s basal plate (Berglin & Gatenholm, 2003; Wiegemann & Watermann, 2003). Barnacles exhibiting any “clouding” of the
basal plate when viewed from below were designated as having the atypical or “cupped” morphology, with all others being designated “flat”. The rate of occurrence of atypical basal plates was determined for each slide, and compared via a one-way ANOVA.

**Results**

*Critical removal stress for PDMSdp125 vs Sylgard 184™*

Only 44% of the barnacles removed from Sylgard 184 exhibited complete release from the surface, without leaving all or part of the basal plate on the surface of the coating. By contrast, 87% of the barnacles removed from PDMSdp125 exhibited complete release from the surface. Mean critical removal stresses for barnacles removed from 1 mm thick coatings of Sylgard 184™ and PDMSdp125 were 0.10 ± 0.02 MPa and 0.069 ± 0.007 MPa, respectively; although technically not significant (one-factor ANOVA; \( n = 21, F = 4.11, p = 0.057 \)) the \( p \)-value was only marginally higher than a 0.050 critical value.

*Occurrence of atypical basal plate and adult cement morphology*

The formation of atypical basal plates and adult cement were observed on all coatings tested (see Figure 1). The proportion of individuals with the atypical morphology was significantly different among coatings of different thickness (one-factor ANOVA; \( n = 15, F = 3.9, p < 0.05 \)) (Figure 2). The lowest frequency of occurrence was on the 0.5 mm coating. The atypical morphology was observed in essentially equal frequency on the thinnest (0.1 mm) and thickest (2.0 mm) samples. Many of the individuals displayed an “intermediate” morphology; that is, the basal plate had the cupped appearance in the centre and a flat morphology closer to the perimeter (Figure 1C). The reverse situation was not observed.

*Growth rate and size as a function of coating thickness*

Growth rate, as measured by the increase in basal plate area, did not differ among coating thicknesses (see Figure 3). Likewise, the areas of basal plates on the three thicknesses were statistically indistinguishable throughout the three months of the experiment (one-factor ANOVA; \( n = 13, F = 0.52, p = 0.61 \)) (Figure 4A). The size of individuals with “cupped” basal plates was not significantly different from individuals with “flat” basal plates (two-factor ANOVA; \( n = 37, \) thickness \( F = 1.23, p = 0.30 \); morphology \( F = 0.04, p = 0.83 \)) (Figure 4B).

**Critical removal stress as a function of coating thickness**

Critical removal stress was significantly different and inversely proportional to coating thickness (one-factor ANOVA; \( n = 44, F = 6.681, p = 0.0031 \)) (Figure 5). The average critical removal stress was \( 0.093 \pm 0.008 \) MPa, \( 0.074 \pm 0.005 \) MPa, and \( 0.055 \pm 0.006 \) MPa on 0.1 mm, 0.5 mm, and 2 mm thick coatings, respectively. A post hoc test showed a significant difference in critical removal stress between 2 mm and both 0.5 mm and 0.1 mm, but not between 0.1 mm and 0.5 mm (Figure 5A). The data also show a lower critical removal force for barnacles with an atypical basal plate than for barnacles with a typical basal plate (two-factor ANOVA: \( n = 44, \) thickness, \( F = 7.437, p = 0.0019 \); basal plate morphology, \( F = 4.182, p = 0.0478 \); interaction, \( F = 0.478, p = 0.6338 \)) (Figure 5B).

**Discussion**

*Growth rate and size as a function of coating thickness*

The hypothesis that the growth rate of the basal plate might differ significantly among coating thickness was not supported (Figures 3 and 4). However, using the basal plate area as a proxy for growth does not take into account the actual mass of the animal. Thus differences among barnacles growing on different thicknesses may not have been detected.

*Occurrence of atypical basal plate and adult cement morphology*

The appearance of atypical basal plates and adult cement has been observed when barnacles grow on silicone coatings (Watermann et al. 1997, Berglin & Gatenholm, 2003; Wiegemann & Watermann, 2003; Holm et al. 2005; Kavanagh & Swain, personal communication) (Figure 1). Individuals exhibiting the atypical morphology were observed to synthesise a thick, paste-like cement that was granular in nature, which was similar to the atypical morphology reported by Berglin and Gatenholm (2003). The exact mechanism by which silicone coatings disrupt the typical process of basal plate growth and adult cement formation is not understood. Sun et al. (2004) suggest that atypical basal plate morphology may form as a result of increased production of adhesive as animals try to maintain contact with a PDMS substratum. Berglin and Gatenholm (2003) showed using electron probe microanalysis and infrared spectroscopy that calcium was incorporated as calcite in barnacles with typical basal plate and adult cement morphology grown on polymethylmethacrylate; in contrast, no
Figure 1. Examples of the various morphologies of a barnacle basal plate grown on an elastomeric surface. A = typical or “flat” morphology; B = atypical or “cupped” morphology; C = transitional basal plate exhibiting both “cupped” and “flat” characteristics.

calcium could be detected in the adult cement of animals with the atypical morphology grown on a polydimethylsiloxane (silicone) coating. In the same study the authors did not report on the frequency of occurrence of the atypical morphology in their experiments. The present results showed that some individuals grown on silicone coatings exhibit the typical basal plate and adult cement morphology. It was also observed that individuals may initially have an atypical (“cupped”) morphology, but then change to the typical (“flat”) morphology as the animal grows. Holm et al. (2005) have demonstrated genetic underpinnings that at least in part determine the frequency of occurrence of the atypical morphology. In their experiments different genetic families of the barnacle B. amphitrite exhibited different rates of occurrence of the atypical morphology when grown on the same silicone coatings. That a monotonic relationship between coating thickness and occurrence of the atypical morphology was not found suggests that coating thickness (and therefore effective compliance) does not directly influence the frequency of occurrence of the atypical morphology (Figure 2).
Critical removal stress as a function of coating thickness

The results showed that critical removal force decreased as a function of coating thickness, although not as $1/h^{1/2}$, where $h$ is coating thickness, as predicted by Kendall (1971) for pull-off removal. There are several reasons why this particular power-law behaviour might not apply to shear of barnacles. First, no theoretical model of shear currently exists that predicts a $1/h^{1/2}$ behaviour. Secondly, the deviation could be an experimental artifact, e.g. due to the application of non-shearing forces (e.g. torque). In addition, Chaudhury has calculated the thickness dependence of the shear removal stress for both solid and flexible plates attached to elastomeric coatings (Chaudhury, personal communication, 2005). He found that the thickness dependence weakened as the flexibility of the plate decreased to that of the coating. The present results also show that the removal stress was lower for barnacles with atypical basal plates than for barnacles with typical basal plates (Figure 5B). These data suggest that the functionality of the adhesive has been compromised in some capacity, which is consistent with the observations and data of Berglin and Gatenholm (2003) and Sun et al. (2004).

Basal plate breakage during removal in shear

It is known that on non-easy release surfaces the basal plates of barnacles will often fracture as animals are dislodged. If the integrity of the basal plate is compromised during removal, then it is likely that the adhesion between the surface and the barnacle cement is so great that the basal plate cannot support the forces needed to dislodge the animal. As the animal grows, the basal plate structural integrity increases (e.g. Berglin et al. 2001). Berglin et al. (2001) showed a gradual transition during barnacle growth in failure mode, viz. i) the smallest barnacles showed a total cohesive failure leaving the entire basal plate on the surface, ii) as the animals grew they shifted to a mixed failure mode where a portion of the basal plate is removed (i.e. breaking of the basal plate), and iii) complete removal of the barnacle
including the entire basal plate, indicating failure of the adhesive bond to the surface. This transition, which they suggest is a measure of the balance between the cohesive strength of the barnacle basal plate and the adhesion bond to the surface, occurs earlier (i.e. for smaller barnacles) on better performing foul-release surfaces. Earlier observations of Singer et al. (2000) showed that the barnacle *B. improvisus* often broke during removal in tensile from Sylgard 184\textsuperscript{TM}. In the present study with *B. amphitrite* a similar situation was observed; only 44% of the barnacles grown on Sylgard 184\textsuperscript{TM} were removed from the surface without cohesive failure, whereas animals of the same size grown on PDMSdp125 showed 87% complete removal. In the coating thickness experiment using only PDMSdp125 coatings total cohesive failure was never observed and greater than 90% of the animals showed failure of the adhesive bond to the surface (i.e. complete basal plate removal). These data clearly demonstrate i) that not all silicone coatings are easy release, and ii) that a pure PDMS such as PDMSdp125 can be easy release without additives such as oils.
Summary
No relationship was found between coating thickness and the rate of growth or the size of barnacle basal plates. There was additionally no discernable relationship between coating thickness and the occurrence of atypical basal plate and adult cement morphology (i.e. “cupped” vs “flat”). Critical release stress qualitatively obeyed fracture mechanics model, i.e. release force decreased with increasing thickness in confinement regime. Indeed, critical removal stress was significantly lower on 2 mm coatings than on either 0.1 mm or 0.5 mm coatings. Moreover, critical removal stress was lower for barnacles with atypical basal plates than for barnacles with typical basal plates. Although 2 mm is thicker than is practical for most commercial coatings, the data demonstrate that coating thickness is an important parameter governing removal of barnacles from elastomeric coatings; coating thickness should be considered when optimising the design of elastomeric foul-release surfaces.

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