Incorporation of silicone oil into elastomers enhances barnacle detachment by active surface strain

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\textbf{ABSTRACT}
Silicone-oil additives are often used in fouling-release silicone coatings to reduce the adhesion strength of barnacles and other biofouling organisms. This study follows on from a recently reported active approach to detach barnacles, which was based on the surface strain of elastomeric materials, by investigating a new, dual-action approach to barnacle detachment using Ecoflex\textsuperscript{®}-based elastomers incorporated with poly(dimethylsiloxane)-based oil additives. The experimental results support the hypothesis that silicone-oil additives reduce the amount of substratum strain required to detach barnacles. The study also de-coupled the two effects of silicone oils (ie surface-activity and alteration of the bulk modulus) and examined their contributions in reducing barnacle adhesion strength. Further, a finite element model based on fracture mechanics was employed to qualitatively understand the effects of surface strain and substratum modulus on barnacle adhesion strength. The study demonstrates that dynamic substratum deformation of elastomers with silicone-oil additives provides a bifunctional approach towards management of biofouling by barnacles.

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Silicone oil; elastomers; barnacle; surface strain; biofouling management

\textbf{Introduction}
Surfaces submerged in natural seawater can be exposed to the settlement of various soft-fouling organisms (eg bacteria and algae) as well as hard-bodied organisms (eg barnacles and molluscs). Biofouling on synthetic surfaces has various deleterious effects, for example in the naval industry, because it leads to economic and environmental drawbacks (Aftring & Taylor 1979; Characklis 1981; Callow & Callow 2002; Bax et al. 2003; Schultz et al. 2011). Surface coatings used to mitigate biofouling can be broadly categorized into two types: antifouling (AF) and fouling-release (FR) coatings. AF coatings (eg self-polishing paints) function by releasing chemically active biocidal compounds which can kill adherent organisms or inhibit the settlement of organisms (Rittschof 2000; Almeida et al. 2007; Sonak et al. 2009). In contrast, FR coatings typically work by reducing the adhesion strength of the fouling organisms on the surface so that the organisms can be easily removed by hydrodynamic stress during navigation or by gentle mechanical cleaning (Baier 1970; Callow & Fletcher 1994; Schultz et al. 1999; Chaudhury et al. 2005; Hearin et al. 2015). Due to the increased environmental concerns and regulations on the use of biocide-releasing paints (eg CuO) (Bryan et al. 1986; Thomas & Brooks 2010; Earley et al. 2014), non-toxic FR coatings have become desired environment-friendly alternatives for biofouling management in marine environments (Callow & Callow 2011).

Researchers have attempted to develop new approaches to control biofouling using a wide range of different strategies. Examples include incorporation of silicone-oil additives (Truby et al. 2000; Kavanagh et al. 2003; Stein et al. 2003; Xiao et al. 2013), engineered biomimetic surface topographies (Carman et al. 2006; Scardino et al. 2008), modification with amphiphilic copolymers (Krishnan et al. 2006; Martinelli et al. 2008; Shivapooja et al. 2012), and tethering of bioactive polymeric moieties (Fan et al. 2005; Zhang et al. 2009; Majumdar et al. 2011; Wang et al. 2014). Among non-toxic FR approaches, poly(dimethylsiloxane) (PDMS) based silicone elastomers have received...
much attention due to their non-toxic and ‘non-sticky’ properties. The FR properties of silicones are mainly attributed to their low surface energy (Kendall 1971), smoothness, reduced polar interaction at their interfaces (Brady & Singer 2000) and inhibition of the curing of biological adhesives (Rittschof et al. 2011).

Shivapooja et al. (2013) and Levering et al. (2014) reported a bioinspired approach for biofouling management, which is based on the concept of active surface deformation of stretchable elastomers. In this method, stretchable silicone elastomers that were fouled with a variety of organisms were dynamically strained using external stimuli (eg direct mechanical stretching, electrical field or pneumatic pressure) to achieve detachment of both bacterial biofilms and barnacles. The amount of strain required for FR was dependent on the mechanical properties of the substratum and the biofouling layer. It was observed that the substratum strain required for the detachment of barnacles was many times higher than that for bacterial biofilms. For instance, detachment of adult barnacles from PDMS required a substratum strain of ≈100%, whereas bacterial biofilms (=75 μm thickness) were effectively detached using a critical strain as low as 5% (Shivapooja et al. 2013). The higher substratum strain required for barnacle detachment is likely due to a combination of their different attachment geometry and the greater adhesion strength of barnacle glue compared to that of slimy bacterial biofilms (Callow & Callow 2002).

Barnacle and crustacean fouling species discharge a variety of biological adhesives, which affix onto surfaces and can cure in water (Naldrett & Kaplan 1997; Brady & Singer 2000; Sun et al. 2004). Barnacles are a major target in biofouling management and a primary invertebrate model for biofouling studies in both laboratory and field environments because of their common occurrence as problematic marine foulers and their tenacious adhesion (Holm 2012; Kamino 2013). Silicone-oil additives are often used in FR coatings because the oil additives passively elute to the surface through the porous silicone elastomer and enhance surface slipperiness, which decreases the coefficient of friction and favors easier release of fouling organisms (Milne 1977; Nevell et al. 1996; Hoipkemeier-Wilson et al. 2004). The mobile (‘free’) silicone-oil compounds on the elastomer surfaces are also known to alter the enzymatic curing process of the secreted adhesives and lower their adhesion strength. In the case of barnacles, Rittschof et al. (2011) reported that silicone oils that elute to the surface significantly alter enzymatic (transglutaminase) activity and alter the cross-linking of glue proteins. Both the above surface actions (ie enhancement of surface slipperiness and inhibition of enzymatic cross-linking) are advantageous in mitigation of biofouling. Though potential deleterious effects of oils leaching from coatings on marine and benthic organisms have been pointed out, there is no statistical evidence to support these concerns (Nendza 2007; Lejars et al. 2012). Truby et al. (2000) reported that the oil leached from a silicone coating was < 1.1 wt% over a period of one year in the laboratory environment.

While the incorporation of silicone-oil additives reduces the adhesive strength of fouling-species (Swain & Schultz 1996; Watermann et al. 1997), it is still a challenge to reduce barnacle adhesion strength to a level such that a small amount of external force (eg hydrodynamic dragging force) can easily detach (‘shear-off’) the barnacles (Wendt et al. 2006). It is also impractical to impregnate a large amount of silicone oil into the coating because it would compromise the durability of the coating, and also might increase detrimental effects of the silicone oils in the ocean environment. Thus, it is desirable to develop more efficient and eco-friendly approaches for easier detachment of barnacles and other fouling species.

This study aimed to use a combination of active surface strain and silicone-oil additives to reduce barnacle adhesion strength, while also reducing the amount of oil required. The study included three specific objectives: (1) to investigate the hypothesis that incorporation of silicone-oil additives into elastomers reduces the amount of substratum strain required for barnacle detachment; (2) to decouple the effect of surface-activity and change in elastomer modulus due to silicone oil on barnacle detachment using substratum deformation; and (3) to qualitatively elucidate the effect of substratum strain and modulus on the barnacle detachment process using fracture mechanics. Ecoflex® silicone-based elastomers and two types of silicone oils were used in the study. Ecoflex was chosen because it is a non-toxic, stretchable silicone and its use for fouling release via active substratum strain was demonstrated in laboratory and field environments by Shivapooja et al. (2015). The adult barnacles (Amphibalanus (= Balanus) amphitrite) used were cultured, grown and reattached on Ecoflex elastomer test surfaces at the Duke University Marine Laboratory (Beaufort, NC, USA). The experimental results support the above hypothesis and demonstrate the effectiveness of this dual-mode approach in the easier detachment of barnacles. The experiment and computation results on the effect of substratum modulus (with and without silicone oil) prove that the surface-activity of silicone oil plays a major role in facilitating detachment of barnacles using surface strain.
Materials and methods

Materials

Ecoflex® 0050 and Silicone Thinner® were purchased from Smooth-On Inc. (Macungie, PA, USA). Ecoflex® 0050 is a platinum catalyst based silicone kit used in the preparation of silicone elastomers, while Silicone Thinner® is a silicone compound additive used for altering the modulus of the silicone elastomers. The chemical formula of Silicone Thinner® is proprietary. The silicone oils used in this study, DMS-T15 (viscosity: 50 cSt, MW: 3,780 g mol\(^{-1}\)) and DMS-T05 (viscosity: 5 cSt, MW: 770 g mol\(^{-1}\)) were purchased from Gelest Inc. (Morrisville, PA, USA). As shown in Table 1, both these oils have identical repeating units of dimethylsiloxane and, structurally, differ only in their molecular weight. For convenience, in the following text, Ecoflex® 0050, DMS-T15 and DMS-T05 are referred to as Ecoflex, oil-T15 and oil-T05, respectively.

Sample preparation

Ecoflex elastomer substrata without silicone-oil additive were prepared using a 1:1 (weight) mixture of the two components (Part-A and Part-B) that comprise the Ecoflex® 0050 kit. This mixture was thoroughly mixed and degassed using a planetary mixer (Thinky-Mixer, Laguna Hills, CA, USA) and then gently poured into a polystyrene Petri dish (90 mm diameter) to obtain a uniform 3-mm thick layer. The sample was then allowed to cure at room temperature for at least 8 h to form a cross-linked elastomer. The cured elastomer was peeled off from the Petri dish and cut into a rectangular shape (70 mm × 40 mm) for use as a test surface. In the preparation of test surfaces with silicone-oil additive, precisely weighed amounts (5 or 10 wt%) of oil-T15 or oil-T05 were added to the Ecoflex precursor mixture before mixing, degassing and curing. Figure 1 summarizes the step-wise procedure used in making the elastomers substrata infused with silicone-oil additives. In the case of Ecoflex with Silicone Thinner®, the silicone-oil additive was substituted with Silicone Thinner®.

Barnacle reattachment on elastomer surfaces

Reattachment of barnacles (Amphibalanus (= Balanus) amphitrite) on the test surfaces was performed using a procedure that is reported elsewhere (Rittschof et al. 2008). In brief, barnacle cyprids were allowed to settle on SilasticT2® coated glass substrata (a gift from North Dakota State University) and cultured for seven weeks to attain adult barnacles with a basal diameter of ≥ 0.5 cm. These adults were used for reattachment on Ecoflex test surfaces. For reattachment, the adult barnacles were carefully pushed off the SilasticT2® surface and immediately placed on the Ecoflex elastomer test surfaces and incubated in air under 100% humidity for a period of 24 h. The test surfaces were then submerged in running seawater and fed with brine shrimp daily for two weeks, after which they were used in barnacle adhesion strength analysis assays.

Barnacle adhesion strength measurements

The adhesion strength between a barnacle and an elastomer substratum was measured following the procedure outlined in ASTM D-5618-94 (ASTM 2011). According to this procedure, a handheld force gauge is used to apply a force parallel to the attachment plane of the barnacle at a rate of ~ 4.5 N s\(^{-1}\) until the barnacle is completely detached from the surface of the elastomer. As the elastomer surface, as cast, was flat, barnacle adhesive was assumed to be in contact with the substratum over the entire basal plate surface and hence, the size of the basal plate was used to determine the attachment area (A) of the barnacle. For this, the baseplate diameter of the detached barnacle was measured in four different orientations using a caliper and then the average diameter (d) was determined for an individual barnacle. The attachment area was then calculated as A = πd\(^2\)/4. Finally, the adhesive strength (kPa) of individual barnacle was calculated by dividing the shear force (F) required to detach the barnacle by its attachment surface area (A).

<table>
<thead>
<tr>
<th>Structural formula of DMS-T15 and -T05 silicone oil</th>
<th>Silicone oil</th>
<th>Viscosity (cSt)</th>
<th>Molecular weight (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Structural formula" /></td>
<td>Oil-T15</td>
<td>50</td>
<td>3,780</td>
</tr>
<tr>
<td></td>
<td>Oil-T05</td>
<td>5</td>
<td>770</td>
</tr>
</tbody>
</table>

Table 1. Structural formula, viscosity and the molecular weight of oil-T15 and oil-T05.
then fit to the neo-Hookean model to obtain the shear modulus of each sample. The average shear modulus for each sample-type was calculated using five identical replicates ($n = 5$).

**Finite element modeling**

The barnacle–elastomer substratum system was simulated as a plane-strain model using the finite-element software package, ABAQUS 6.14 (Dassault Systèmes Simulia Corp., Providence, RI, USA). To capture the essential physical features of the system, the barnacle was assumed to be a rigid body and the substratum was modeled as an incompressible neo-Hookean material (Shivapooja et al. 2013). The shear modulus $\mu_s$ of the substratum was measured by uniaxial tensile testing. The model of the substratum was discretized using hybrid quadratic elements (CPE8MH), and mesh convergence was carried out to verify mesh insensitivity. The thickness of the substratum was taken to be large enough so that the effect of substratum thickness on barnacle detachment was negligible. Due to symmetry, only one half of the barnacle-substratum system was modeled, and therefore a symmetric boundary condition was applied. A prescribed displacement was applied to

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**Cyclic strain of the elastomer substrata**

The elastomer substrata with reattached barnacles were subjected to varying amounts of uniaxial strain (0–50%) using a universal test machine (Test Resources, Shakopee, MN, USA) equipped with a loading frame, modular actuator and computerized controller. The Ecoflex elastomers with reattached barnacles were clamped onto the grips of the equipment and fixed amount (12.5, 25, 37.5 or 50%) of cyclic strain was applied for 15 cycles (see Figure 2) at constant strain rate of 50 mm min$^{-1}$ (±0.5%).

**Measurement of elastomer shear modulus**

The shear moduli of silicone elastomer samples prepared with different compositions were measured using a Micro-Strain Analyzer (MSA, TA Instruments RSA III, New Castle, DE, USA) under uniaxial tension. The elastomers were cut into thin strips (20 mm × 5 mm × 3 mm) and gripped firmly between the clamps of the instrument. Controlled uniaxial tension was applied on the elastomer strips using a preload of 0.01 N and a strain ramp of 0.05% min$^{-1}$. The displacement or stretch rate was set to 1 mm s$^{-1}$. The stress vs stretch data recorded by the instrument were then fit to the neo-Hookean model to obtain the shear modulus of each sample. The average shear modulus for each sample-type was calculated using five identical replicates ($n = 5$).
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uniaxial strain (12.5, 25, 37.5 or 50%) at a constant strain rate of 50 mm min$^{-1}$ using a universal testing machine (Figure 2). After cyclic stretching, the elastomer substrata were unloaded from the grips and the barnacle adhesion strength was measured and analyzed following the standard push off assay according to ASTM D-5618-94 (ASTM 2011).

Figure 3a shows optical images of a barnacle baseplate on Ecoflex elastomer before and after applying a 50% uniaxial strain. Prior to straining, the adsorbed organic matter (ie the adsorbed biofilm or secreted barnacle glue) area around the attached baseplate was stained by exposure to crystal violet dye (2% aqueous). As seen in Figure 3a, when the elastomer is repeatedly stretched to 50% strain (4×), the crystal violet boundary on the substratum (indicated by the red dash-line) was displaced from the barnacle baseplate. This indicates the partial debonding of the barnacle baseplate when the substratum is strained. By considering the barnacle to be a rigid solid on a soft substratum, the de-bonding can be assumed as the inward

de-bonding.

Results and discussion

Effects of silicone oil and cyclic substratum strain on barnacle adhesion strength

The preparation of elastomer substrata and the reattachment of barnacles are detailed in the Methods section. The elastomers were conditioned in flowing seawater for a period of two weeks and then barnacles were reattached and grown on one side of the elastomer substrata for two weeks. The elastomer substrata with reattached barnacles were stretched for 15 cycles to a fixed level of uniaxial strain (12.5, 25, 37.5 or 50%) at a constant strain rate of 50 mm min$^{-1}$ using a universal testing machine (Figure 2). After cyclic stretching, the elastomer substrata were unloaded from the grips and the barnacle adhesion strength was measured and analyzed following the standard push off assay according to ASTM D-5618-94 (ASTM 2011).

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Incorporation of silicone-oil additives can reduce the barnacle adhesion strength on elastomers, and that the amount of reduction is dependent on the amount of silicone oil added. The largest decrease in barnacle adhesion strength (under no substratum strain) was observed to be ≈16%, for 10 wt% oil-T05.

When substratum strain was employed (ie a strain > 0%), the barnacle adhesion strength for all elastomer substratum formulations significantly decreased with an increase in the applied strain (Figure 3b and c). Also, for any given specific strain applied, the barnacle adhesion strength on Ecoflex with silicone-oil additives was substantially lower than on Ecoflex without silicone oil. For instance, after 50% cyclic strain the adhesion strength on Ecoflex without oil additive was ≈45 kPa, whereas on Ecoflex with 5 wt% oil-T15 the barnacle adhesion strength was ≈15 kPa (Figure 3b). Moreover, for any given strain, barnacle adhesion strength reduced with increase in silicone-oil additive concentration (eg from Figure 3b, after 50% cyclic strain, the barnacle adhesion strength on Ecoflex with 10 wt% oil-T15 was reduced to 0 kPa). These results support the hypothesis that incorporation of silicone oils reduces the strains required to detach barnacles. Also, by comparing Figure 3b and c, it is apparent that barnacle adhesion strength (at strain > 0) was slightly lower (p < 0.05 for any given strain) on Ecoflex with oil-T15 (Figure 3b) than that on Ecoflex with oil-T05 (Figure 3c). This suggests that barnacle detachment under deformation is influenced by multiple factors, including the concentration and the type of silicone-oil additive (Stein et al. 2003). In the experiments presented below, further investigation was limited to oil-T15.

**Effect of elastomer modulus vs silicone oil on the substratum strain needed to detach barnacles**

Incorporated silicone-oil additives are known to affect the mechanical properties of elastomers, and thereby can reduce the durability of coatings (Truby et al. 2000). This is one of the primary reasons that coating companies restrict the concentration of silicone-oil additives in commercial FR coatings to < 20 wt% (Nendza 2007). Several researchers have reported that the modulus of the silicone influences the adhesion strength (Brady & Singer 2000; Kim et al. 2007), the base-plate geometry (Sun et al. 2004) and the glue morphology of attached barnacles (Ahmed 2007).
et al. 2014). To the authors' knowledge, however, there has been no quantitative study on the effect of a change in substratum modulus due to incorporated silicone oils on barnacle adhesion strength. Hence, in this study the effect of silicone oils on the modulus of an elastomer (Ecoflex) was determined, and then Ecoflex elastomers without silicone-oil additives but a matching modulus were prepared by using Silicone 'Thinner' additive (Smooth-On) (see Figure 4a). According to the manufacturer, Silicone Thinner® covalently bonds within the Ecoflex precursor mixture and modifies the modulus of Ecoflex. The change in modulus depends on the amount of Silicone 'Thinner' added. Unlike the silicone oil additives (eg oil-T15 or oil-T05), Silicone Thinner® becomes part of the cross-linked Ecoflex elastomer matrix and does not easily leach from the surface.

Figure 4a shows the change in the Ecoflex modulus for different concentrations of oil-T15 and Silicone Thinner® additives, measured after conditioning in seawater for a period of two weeks (see Methods section). These data show that the modulus of Ecoflex was reduced with an increase in additive (Silicone Thinner® or oil-T15) concentration. The modulus of Ecoflex with 5 wt% oil-T15 was 35.7 kPa, which closely matches with Ecoflex containing 2 wt% Silicone Thinner®. Likewise, the modulus of Ecoflex with 10 wt% oil-T15 was 30.8 kPa, which matches with Ecoflex containing 6.5 wt% Silicone Thinner®. The Ecoflex elastomers with 2 and 6.5 wt% Silicone Thinner® were used as control samples to examine how oil-T15 affects elastomer modulus and thus barnacle adhesion strength.

Using the procedure detailed in the Methods section, barnacles were reattached and grown on multiple replicates of Ecoflex elastomer with 2% and 6.5% Silicone Thinner®. The adhesion strength of barnacles was measured on these surfaces before and after application of cyclic substratum strain. The experimental results are summarized in Figure 4b. It can be observed that without deformation (ie 0% strain), the barnacle adhesion strength on Ecoflex decreased slightly (< 5%) upon incorporation of Silicone Thinner®. When substratum deformation was applied (12.5–50% strain), the barnacle adhesion strength substantially decreased with an increase in the strain on all substrata. Moreover, for any given strain (> 0%), the barnacle adhesion strength was lower on Ecoflex without Silicone Thinner®, and increasing amounts of Silicone Thinner® resulted in less decrease in adhesion strength relative to the unstrained control. This indicates that incorporation of Silicone Thinner® increased the amount of substratum strain needed to detach barnacles. Given that Silicone Thinner® lowers the modulus of Ecoflex (Figure 4a) and under the assumption that Silicone Thinner® has minimal effect of surface activity on barnacle glue properties, the results from Figure 4b suggest that a softer substratum (ie a lower modulus) requires a larger amount of substratum strain to detach barnacles.

Since the moduli of Ecoflex with 2 and 6.5 wt% Silicone Thinner® match with those of Ecoflex with 5 and 10 wt% oil-T15, respectively (see Figure 4a), a comparison of data in Figures 2b and 4b allows quantitative de-coupling of the two major effects (ie substratum modulus and surface-activity) of silicone oils on barnacle adhesion strength. This comparison is shown in Figure 4c in terms of the percentage decrease in barnacle adhesion strength compared to the unstrained Ecoflex control. That is, the percentage values were calculated by considering the barnacle adhesion strength on Ecoflex alone (ie without Silicone Thinner® oil-T15, or applied substratum strain) as a reference. With no substratum deformation (ie 0% strain), the barnacle adhesion strength on Ecoflex with Silicone Thinner® decreased by < 5%, whereas on Elastomer with oil-T15 the adhesion strength decreased by 7.5% (for 5 wt% oil-T15) and 16% (for 10 wt% oil-T15). This implies that, in the absence of deliberate substratum deformation, the decrease in barnacle adhesion strength due to silicone oil was partly contributed by a decrease in the elastomer modulus and partly by surface-activity (eg inhibition of enzymatic curing of bioadhesives of oil at the surface).

When substratum deformation (cyclic strain > 0%) was applied (Figure 4c), the percentage decrease in barnacle adhesion strength was higher on Ecoflex without additives than on Ecoflex with Silicone Thinner®. For instance, after 50% cyclic strain, the barnacle adhesion strength on Ecoflex (without oil or Silicone Thinner® additive) was decreased by 47%, but for Ecoflex with 6.5 wt% Silicone Thinner® it was decreased by only 30%. Also, for any given strain, the decrease in barnacle adhesion strength was highest on Ecoflex with oil-T15. Taken together, this comparison suggests that a decrease in the elastomer modulus (due to silicone oils) increases the strain required to detach barnacles, while the surface-activity of silicone oils substantially reduces the barnacle adhesion strength upon substratum deformation so that the overall strain required to detach barnacles is lowered.

**Finite-element model for barnacle detachment using substratum deformation**

Fracture-mechanics models have been used to study the forces involved in the mechanical debonding of bioadhesives. Kendall (1971), Chung and Chaudhury (2005) and others considered pseudo-barnacles (ie rigid studs glued to test surfaces) to gain insight into the fracture mechanics involved in the detachment of barnacles. In those studies, the barnacle detachment force was applied perpendicular to the surface, which leads to a tensile-mode crack. This model is not applicable here.
Figure 4. Effect of substratum modulus and substratum deformation on barnacle adhesion strength. (a) Variation in the shear modulus of Ecoflex with addition of different wt% of Silicone Thinner® and oil-T15 additives. The substratum moduli (dashed lines) of Ecoflex with 5 and 10 wt% oil-T15 match those with 2 and 6.5 wt% Silicone Thinner®, respectively. The error bars represent SDs of the mean (n = 5). (b) Barnacle adhesion strength on Ecoflex containing 0, 2, and 6.5% Silicone Thinner® as a function of applied strains. (c) The percentage decrease in barnacle adhesion strength from 80.5 kPa for elastomer without oil additive, with oil-T15 and with Silicone Thinner® at 0%, 12.5% and 50% substratum strains. 80.5 kPa corresponds to the adhesion strength of barnacle on unmodified Ecoflex (ie without Silicone Thinner® oil-T15, or applied substratum strain). The errors bars in (b) and (c) represent SDs of the mean (n = 15) and * represents p < 0.01.
because the current study is based on shear-mode cracks, generated by applying a force parallel to the substratum surface. To better understand the effect of substratum modulus and applied strain on barnacle detachment, a finite-element model was developed to calculate the energy release rate during the strain-enhanced detachment process. The energy release (i.e., the decrease in the system’s elastic energy when the crack propagates per unit area) is affected by the elastic mismatch, the barnacle contact area and the lengths of the cracks generated at the barnacle-substratum interface. Considering a 2-D plane-strain model as shown in Figure 5a, when strain is applied to the elastomer substratum, it is assumed that two cracks develop at the periphery of the interface between the barnacle baseplate and the elastomer surface, and symmetrically propagate inward with increase in substratum strain (the 2-D schematic in Figure 5a has resemblance to digital photographs of barnacle base plate shown in Figure 3a). The crack-propagation happens when the decrease in the interfacial elastic energy due to the applied strain exceeds the adhesion energy between the barnacle and the elastomer (Lu et al. 2007). As shown in the calculated strain distribution in the elastomer substratum (Figure 5b), the crack tip has a high stress and strain concentration, which suggests that crack is initiated from the edge of the barnacle baseplate. Since the baseplate of the barnacle is stiffer than the elastomer substratum, the barnacle is assumed to be a rigid material (Kendall 1971). The energy release rate \( G \) for crack propagation at the interface of barnacle and strained elastomer substratum (Shivapooja et al. 2013) can be expressed as

\[
G = \mu_s L_s f(\varepsilon_{\text{app}}, L/L_s)
\]

(1)

where \( \mu_s \) is the shear modulus of the elastomer substratum, \( L \) is the length of the barnacle baseplate adhered on the substratum, \( L_s \) is the length of the substratum at 0% strain, \( \varepsilon_{\text{app}} \) is the applied strain upon active deformation and \( f \) is...
a non-dimensional function obtained through the finite-element method. This model can be used to elucidate the effect of the applied strain and the substratum modulus on the detachment of barnacles from substratum surfaces via the active strain method. Taking a small crack \((a/L = 1\%)\) as an example, it is apparent from Equation 1 and Figure 5c that for a given specific strain, a stiffer substratum will generate a larger energy release rate, i.e., a rigid substratum will be more efficient in releasing the barnacles. This is in agreement with the experimental results for Ecoflex with Silicon Thinner® (Figure 4a and b). However, in the case of Ecoflex with silicone oil additive (Figure 4c), the trend is reversed and this model fails. This is because the model does not account for the effect of the surface-activity of the silicone oils (e.g., the effect of silicone oil on the enzymatic curing process of barnacle glue).

Figure 5d shows the normalized energy release rate \((G^*)\) as a function of crack size, \(a/L\), for different amounts of substratum strain. The energy release rate was normalized with respect to the energy release rate at zero crack length and 100% strain. The interfacial crack propagates when the energy release rate exceeds the value of adhesion strength of barnacle on the surface (Lu et al. 2007; Shivapooja et al. 2013). This implies that for a fixed amount of substratum strain, the barnacle will not debond at the edge if the adhesion strength is below the curve in Figure 5d. Additionally, it can be seen from Figure 5d that the energy release rate decreased with an increase in the crack length \((a)\). This suggests that the larger the barnacle baseplate \((L)\), the easier it will be to detach the barnacle using substratum strain (a prediction that is beyond the scope of this study). It can also be observed (Figure 5d) that for a specific crack length, \(a/L\), larger amount of applied strain leads to higher energy release rate and thus, it is easier to detach the barnacle.

To sum up, this model provides a qualitative interpretation of surface-deformation induced debonding of barnacles. Although this model can be used to interpret the effect of substratum modulus and crack length on barnacle detachment using surface strain, it does not account for the surface-activity effects of any incorporated silicone oils.

In conclusion, adding silicone oils into elastomers can substantially reduce the amount of strain needed to detach barnacles. Thus, this report provides a potential, new, bifunctional approach to mitigate biofouling in marine and biomedical (Levering et al. 2016) applications. The use of surface deformation for biofouling management has been already demonstrated (using electro-actuation (Shivapooja et al. 2013) and pneumatic-actuation (Shivapooja et al. 2015) techniques) and the use of silicone-oil additives may improve such approaches.

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