Biofouling, 2005; 21(1): 41 – 48

Taylor & Francis
Taylor & Francis Group

The influence of elastic modulus and thickness on the release of the soft-fouling green alga *Ulva linza* (syn. *Enteromorpha linza*) from poly(dimethylsiloxane) (PDMS) model networks

MANOJ K. CHAUDHURY[2], JOHN A. FINLAY[1], JUN YOUNG CHUNG[2], MAUREEN E. CALLOW[1] & JAMES A. CALLOW[1]

[1]*School of Biosciences, University of Birmingham, Birmingham, UK, and* [2]*Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania, USA*

(Received 13 October 2004; accepted 23 December 2004)

Abstract
The effect of modulus and film thickness on the release of adhered spores and sporelings (young plants) of the green fouling alga *Ulva* (syn. *Enteromorpha*) was investigated. PDMS elastomers of constant thickness (100 μm) but different elastic moduli were prepared by varying cross-link density with functional silicone oligomers with degrees of polymerization ranging from 18 – 830. This provided a 50-fold range of modulus values between 0.2 and 9.4 MPa. Three PDMS coatings of different thicknesses were tested at constant elastic modulus (0.8 MPa). The data revealed no significant increase in percentage spore removal except at the lowest modulus of 0.2 MPa although sporelings released more readily at all but the highest modulus. The influence of coating thickness was also greater for the release of sporelings compared to spores. The release data are discussed in the light of fracture mechanics models that have been applied to hard fouling. New concepts appertaining to the release of soft fouling organisms are proposed, which take into account the deformation in the adhesive base of the adherand and deformation of the PDMS film.

Keywords: Ulva*, spores, green algae, adhesion, foul-release, PDMS, elastic modulus*

Introduction

The fouling of underwater structures, and ships' hulls in particular, results in increased operational and maintenance costs (Townsin, 2003). Toxic antifouling paints containing copper and other biocides have provided an effective control of many fouling species, but these are now under scrutiny due to environmental concerns. Novel, environmentally benign solutions to control biofouling are therefore sought and a prominent approach is to use a coating that minimizes adhesion between the organism and the coating, promoting release of the accumulated fouling as a result of the hydrodynamic forces generated by movement through the water (Swain, 1999; Schultz et al. 2003). Commercially available 'fouling-release coatings' are based on silicone elastomers formed from polymerized dimethylsiloxanes (PDMS). The surface property most frequently correlated with resistance to adhesion is the critical surface tension for wetting (γ_c) (e.g. Baier, 1973; Becka & Loeb, 1984) and it is generally accepted that the low critical surface tension of silicone elastomers [approximately 23 mNm^{-1} (Brady & Singer, 2000)] is a major determinant in the low adhesion, fouling-release properties of these polymers.

More recently the concepts of fracture mechanics, as described in Kendall's model (Kendall, 1971), have been applied to the analysis of fouling-release behaviour. In this model, the pull-off force (F) required to remove a rigid cylindrical stud of radius a, from an elastomeric film of thickness h, is given by:

$$F = \pi a^2 (2WK/h)^{1/2} \quad (1)$$

where W is the work of adhesion or the energy per unit area needed to separate the interface and K is the bulk modulus of the film, which is related to its Young's modulus E by $E/(3(1-2v))$, v being the Poisson's ratio.

Equation 1, however, applies to situations where the contact radius a is much larger than the thickness

Correspondence: James A. Callow, School of Biosciences, University of Birmingham, Birmingham B15 2TT, UK. E-mail: j.a.callow@bham.ac.uk

ISSN 0892-7014 print/ISSN 1029-2454 online
DOI: 10.1080/08927010500044377

of the film. For a small contact radius ($a < h$), the pull-off force is independent of thickness as shown in Equation 2 (Kendall, 1971).

$$F = (8\pi a^3 WE/(1 - \nu^2))^{1/2} \quad (2)$$

It is now apparent that adhesion strength of hard-fouling organisms such as barnacles and 'pseudo-barnacle' epoxy studs is also influenced by coating modulus (Brady & Singer, 2000; Berglin et al. 2003; Stein et al. 2003), and thickness (Kohl & Singer, 1999; Singer et al. 2000) as well as critical surface tension. Newby and Chaudhury (1997) have also demonstrated that release is a function of friction and slippage. However, this understanding of the fouling-release mechanism has been developed for macroscopic, 'hard foulers' where the modulus and size of the adherand is significantly larger than the modulus and thickness of the coating. Where these conditions do not pertain then macroscopic fracture models may be inappropriate. In particular there is a need to examine the importance of these parameters in the context of soft-fouling organisms such as spores and young plants of marine algae, whose dimensions and compliance are totally different to hard foulers. The purpose of this paper is to report the outcome of such a study, using the green alga *Ulva* [syn. *Enteromorpha*, (Hayden et al. 2003)], as a model for soft-fouling organisms.

Ulva is a genus of common, green macroalgae found throughout the world in the upper intertidal zone of seashores and as a fouling organism on a variety of man-made structures including ships' hulls (Callow, 1996). Dispersal is achieved mainly through asexual zoospores, quadriflagellate, pear-shaped cells, 5–7 μm in length. Colonization of substrata involves the transition from a free-swimming spore to an adhered non-motile spore (Callow et al. 1997), adhesion being achieved via the secretion of a liquid glycoprotein adhesive which on release forms a discrete gel-like pad on the surface (Callow et al. 2003). Spores often settle gregariously, i.e., spores settle in close proximity to previously settled spores, to form groups or rafts of cells.

Materials and methods

Settlement and adhesion assays with Ulva *zoospores*

Fertile plants of *Ulva linza* were collected from Wembury Beach, England (50°18′ N; 4°02′W). Zoospores were released and prepared for attachment experiments as described in Callow et al. (1997). Ten ml aliquots (1.5 x 10^6 spore ml^{-1}) were pipetted into individual compartments of polystyrene culture dishes (Fisher), each containing either a control glass microscope slide (acid-washed in a 50% methanol/50% concentrated hydrochloric acid mixture, followed by 100% concentrated hydrochloric acid (2 h in each), or a glass slide coated with PDMS. Six replicate dishes were incubated in the dark for 1 h before the slides were washed by passing backward and forward ten times through a beaker of seawater, in order to remove unattached spores.

Three replicate slides from each treatment were fixed in 2% glutaraldehyde in seawater and processed as described in Callow et al. (1997). The remaining three replicates were placed in a flow apparatus (Schultz et al. 2000) that had been modified by fitting a higher capacity pump as described in Finlay et al. (2002b). Slides were exposed to a fully-developed turbulent flow for 5 min at 55 Pa wall shear stress. After fixing slides in 2% glutaraldehyde, adhered spores were visualized by autofluorescence of chlorophyll and quantified by image analysis as described in Callow et al. (2002). Thirty counts were taken at 1 mm intervals along the middle of the long axis of each of the three replicate slides. The mean number of spores remaining attached to the surface after exposure to turbulent flow was compared with the mean number before the slides were subjected to flow. Since the level of settlement in each experiment was different (e.g. because different spore batches were used), data are presented in terms of percentage spore removal compared with the controls, $\pm$ standard errors calculated from arcsine-transformed data. Data were subjected to one-way ANOVA and the means compared using the Tukey test (Fowler & Cohen, 1991).

Adhesion assays with Ulva *sporelings*

Experiments were also conducted on sporelings, i.e., young plants that develop from attached spores. Zoospores were obtained from mature *Ulva* plants and diluted to produce a zoospore suspension of 0.1 (OD 660 nm) and settled onto coated slides as described above. After 1 h the slides were gently washed in seawater to remove unattached zoospores and placed in clean dishes with 10 ml of enriched seawater medium (Starr & Zeikus, 1987). Dishes were incubated in a growth cabinet (Sanyo MLR-350) at 18°C with a 16:8 light:dark cycle (photon flux density 330 μmol $m^{-2}s^{-1}$). The medium was refreshed every 2 d. Biomass was estimated at 8 d by extraction of chlorophyll *a*. The sporelings were removed from half of each slide and chlorophyll *a* extracted in dimethyl sulphoxide (DMSO) (Shoaf & Lium, 1976). The chlorophyll *a* concentration was determined spectrophotometrically using the equations of Jeffrey & Humphrey (1975) and data expressed as weight of chlorophyll *a*/unit area of test surface. The biofilm on the other half of each slide was left intact.

To assess the strength of adhesion of the sporelings, the slides, with the second half of the sporelings attached, were exposed to a shear stress of 55 Pa in a water channel for 5 min (Schultz et al. 2000). The biomass remaining was manually removed and the chlorophyll *a* content determined as above. The water channel produced fully developed turbulent flow similar to that experienced around the hull of a ship traveling at 15 knots.

Preparation and characterization of PDMS coatings

For a list of abbreviations, see Table I. Poly(dimethylsiloxane) (PDMS) coatings used in these experiments were model silicone elastomer networks bonded to glass microscope slides (Corning microslides, 25 mm × 75 mm × 1 mm).

The glass slides were first cleaned in hot piranha solution for 30 min, and then thoroughly rinsed in distilled/deionized water. After blow-drying the slides in pure nitrogen gas, they were further cleaned in a Harrick plasma cleaner (model PDC-23G, 100 W) at a pressure of 0.2 Torr for 45 s. The materials used for the preparation of cross-linked PDMS networks were vinyl terminated dimethylsiloxane oligomers ($H_2C=CH(Si(CH_3)_2O)_nSi(CH_3)_2CH=CH_2$) of different molecular weights, platinum catalyst (Dow Corning Syloff 4000), maleate inhibitor (Dow Corning Syloff 7694), and the methylhydrogen siloxane cross-linker (Dow Corning Syloff 7678: $(H_3C)_3O-(SiHCH_3O)_p(Si(CH_3)_2O)_qSi(CH_3)_3$, M_n and $M_w = 3.5$ and 7.5 kg mol^{-1}, respectively).

The oligomers, catalyst, and inhibitor were first mixed thoroughly with the mass ratio of 97.4: 1.9: 0.7 for all molecular weights before adding the cross-linker. The proportional amount of cross-linker added after thorough mixing varied with molecular weight as $23M^{-0.97}$, where M is in kg mol^{-1} (M being the number average molecular weight, M_n,). The mixtures were poured on the thoroughly cleaned and plasma oxidized glass slide, and were covered by a second glass slide coated with a low energy self-assembled monolayer (SAM) of hexadecyl trichlorosilane ($HC,CH_3(CH_2)_{15}SiCl_3$, United Chemicals Technologies, Inc.).

The mixture within the two microscope slides was then cross-linked in a pre-heated convection oven at 120°C for 50 min by the platinum catalyzed hydrosilation reaction, which involves an addition reaction between vinyl groups of the dimethylsiloxane oligomer and the Si-H groups of the siloxane cross-linking agent. This reaction system yielded a highly cross-linked network with negligible by-products. After the PDMS networks were fully cross-linked, the glass slides with the SAM coating were easily removed. All the PDMS networks adhered strongly to the other untreated glass slide, except the PDMS network of $M = 52$ kg mol^{-1}. In order to achieve good bonding for this polymer, the glass slides were modified with a very thin layer of Dow Corning Sylgard 170 (without fillers). A few drops of this polymer were placed on the glass slides and then distributed uniformly with a Kimwipe before adhering the PDMS coating.

Polymer films with uniform and controlled thickness ($h = 16$ μm, 100 μm and 430 μm) were prepared by crosslinking the elastomer between two rigid glass slides separated by two sets of filler gauges (spacers) of known heights (Ghatak et al. 2000). The elastic moduli of the networks were estimated by using the method of contact mechanics (Vorvolakos & Chaudhury, 2003), in which hemispherical PDMS lenses were brought into and out of contact with HC-coated flat silicon wafer as a function of the controlled loads. The analysis of the contact radius as a function of the load yielded the elastic moduli of the cross-linked PDMS networks (summarized in Table II), which are in excellent agreement with those obtained from the AFM measurements reported recently (Sun et al. 2004b).

Table I. List of terms and symbols.

Symbol	Definition
a	Contact radius
E	Elastic modulus
E_a	Modulus of the spore adhesive pad
E_c	Composite modulus of the adhesive and the PDMS film
E_p	Elastic modulus of the PDMS film
F	Pull-off force
h	Thickness of the elastomeric film
K	Bulk modulus
W	Work of adhesion
γ	Surface free energy of substratum
λ	Wavelength of elastic instability in a film
ν	Poisson's ratio
σ	Pull-off stress

Results

PDMS coatings of constant thickness (100 μm) but different elastic moduli, were prepared by varying cross-link density with functional silicone oligomers

Table II. The degrees of polymerization (DP) and molecular weights (M) of vinyl terminated dimethylsiloxane oligomers used to make cross-linked PDMS networks, and the corresponding elastic moduli (E).

DP	M (kg mol^{-1})	E (MPa)
18	1.3	9.4
60	4.4	2.7
253	18.7	0.8
830	52.2	0.2

with degrees of polymerization ranging from 18 – 830. This provided a 50-fold range of modulus values between 0.2 and 9.4 MPa. The settlement of zoospores was not significantly affected by elastic modulus (data not shown). Strength of attachment data is shown in Figure 1. One-way ANOVA followed by individual Tukey tests revealed no significant increase in % removal as the modulus decreased between 9.4 and 0.8 MPa but there was a significant ($p < 0.05$) increase in removal at the lowest modulus of 0.18MPa. Detachment of sporelings from the highest modulus PDMS coating (9.4 MPa) was low but at lower moduli (0.2 and 0.8 MPa) there was a strong and significant ($p < 0.05$) affect of modulus on detachment with 80% removal being achieved on the two softest surfaces (see Figure 1).

Three PDMS coatings of different thicknesses were tested at constant elastic modulus (0.8 MPa). The settlement of zoospores was similar on all PDMS coatings (data not shown). The removal of spores at a wall shear stress of 55 Pa is shown in Figure 2. Removal was relatively low on this type of PDMS at this shear stress and there was no significant difference in removal between the two thinnest coatings (16 and 100 μm). However, the 430 μm coating gave significantly more removal ($p < 0.05$) although the percentage removal was still relatively low. Coating thickness had a greater influence on the removal of sporelings with a significant ($p < 0.05$) increase in removal as thickness was increased from 16 to 100 μm. The growth of sporelings was similar on all thicknesses (data not shown).

Discussion

In considering the effects of coating properties on fouling organisms the effects on settlement, the transition of a spore or larva from the planktonic to the sessile state, may be distinguished from effects on the strength of adhesion of the organism once it has settled. Gray et al. (2002) recently showed that settlement of larvae of several invertebrate species was positively correlated with elastic modulus, an effect which they hypothesized to be due to an influence of the surface on mechano-sensitive ion channels. However, the silicone elastomers prepared by Gray et al. (2002) were extremely soft, with moduli in the range 0.01 to 0.1 MPa [these are corrected values reported in an Erratum Note to the original 2002 paper (Biofouling 19(2), April 2003)]. Since commercial antifouling silicone elastomers such as RTV11 or Intersleek have moduli in the range 3 – 1.4 MPa respectively (Arce et al. 2003) the significance of this observation for marine biofouling is not clear. The moduli of surfaces used in the present paper ranged from 0.2 – 9.4 MPa. In the present study no influence of coating thickness or modulus on the settlement of *Ulva* zoospores was detected.

Since the work of Baier (1973) and Dexter (1979), adhesion of fouling organisms has been correlated with the surface free energy (or the related parameter, critical surface tension) of the substratum. More recently, release of hard-fouling organisms has been interpreted in the light of fracture mechanics models and in the case of barnacles, or 'pseudobarnacle' proxies, adhesion strength is proportional to $(\gamma E)^{1/2}$; where γ is the surface energy and E is the elastic modulus (Brady & Singer, 2000). For this reason, siloxane elastomers are the major commercial candidates for environmentally benign fouling release coatings, as they possess both low modulus and low surface energy (Wynne et al. 2000). Other studies with hard-fouling organisms have demonstrated that thickness of coating also plays an appreciable role in release (Sun et al. 2004a). In

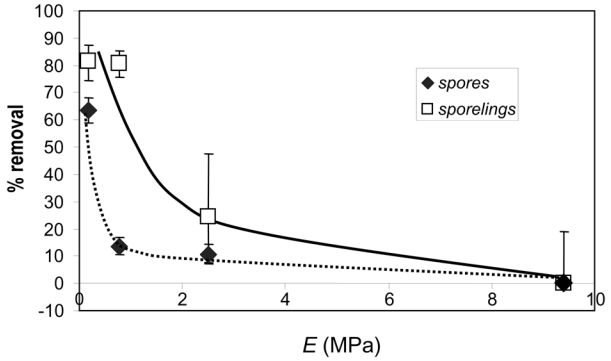

Figure 1. Percent removal of spores and sporelings from PDMS coatings of differing elastic modulus after exposure to shear stress of 55 Pa. All coatings were 100 μm thick. Bars represent standard errors from arcsine-transformed data. The absolute level of spore settlement in the experiment was 1360 ± 133 spores mm^{-2} (mean $\pm$ 2 x SE).

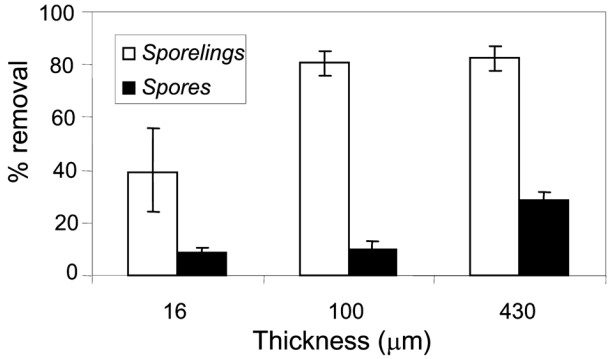

Figure 2. Percent removal of spores and sporelings from PDMS coatings of differing thickness, after exposure to shear stress of 55 Pa. All coatings had the same elastic modulus of 0.8 MPa. Bars represent standard errors from arcsine-transformed data. The absolute level of spore settlement in the experiment was 529 ± 42 spores mm^{-2} (mean $\pm$ 2 x SE).

the case of soft-fouling species, studies on *Ulva* spores using non-polar, self-assembled monolayers, have shown that like hard-foulers, adhesion is strongly influenced by critical surface tension (or 'wettability') (Finlay et al. 2002a).

The addition of relatively high concentrations (20%) of non-network-forming PDMS-based oils to a silicone elastomer (T2 Silastic) resulted in only a small increase in the removal of spores (Hoipkemeier-Wilson et al. 2004). However, to date there has been no examination of the influence of mechanical factors. A series of model network silicone elastomers (i.e. without added fillers) was therefore constructed using functional silicone oligomers of different chain length to influence the cross-linking and thus the modulus of the coating, without introducing any changes to surface energy, and tested the effect of these on the detachment of *Ulva* spores and sporelings.

The experimental analysis of the influence of coating parameters on release of macro-fouling organisms typically employs detachment methods that enable adhesion strengths or critical pull-off forces to be determined for individual specimens. For example, a common approach used for barnacles, tubeworms and oysters is to apply a mechanical shear force parallel to the base of the organism (Swain & Schultz, 1996; Kavanagh et al. 2001; Sun et al. 2004a) while Singer et al. (2000) used a pull-off tester for barnacles and pseudobarnacles.

A different, less direct methodology has to be used for micro-fouling organisms since the adhesion strengths of individual cells cannot be readily determined. The method used here was to impose a hydrodynamic shear stress to spores settled on coated microscope slides in a fully turbulent flow channel. Fully developed channel flows then allow accurate determination of wall shear stresses from a simple pressure gradient measurement (Schultz et al. 2000; 2003). In principle it would be possible to expose replicate samples to a range of such stresses, then to determine critical shear stresses for detachment. Since within a population of settled spores there is a natural between-spore variability in adhesion strength (Finlay et al. 2002b), it would be necessary to measure the shear stress at which, say 50% of cells detach, as a measure of the relative adhesion strength of the population of cells on any specific coating. Such values could then be entered into various quantitative models of the mechanics of adhesion. In practice such an approach is logistically impossible because of the number of samples that would need to be handled. Therefore, the simpler approach had to be adopted in this paper whereby the proportion of attached spores (or sporelings) that were detached on exposure to a single shear force were measured.

Since the contact radius of the spore is much smaller than the thickness of the films used in these studies, the version of the 'Kendall' model described in Equation 2 may seem to be appropriate. However, results with *Ulva* spores using coatings of constant thickness reveal that a change in modulus over an order of magnitude had very little influence on the proportion of spores detached until very soft polymer ($E = 0.2$ MPa) was tested, i.e. the detachment behaviour did not follow that predicted by Equation 2. In order to understand the release behaviour of the spores from the coating surfaces, the deformation in the adhesive pad may need to be considered in addition to the deformation of the film.

However, in order to predict the release force, the mode of delamination of the adhesive pad from the surface first needs to be known. There are, in general, three situations to consider. In the first case, the adhesive is infinitely rigid and the PDMS film is so confined that an elastic instability develops (see Figure 3a) at the interface with the application of

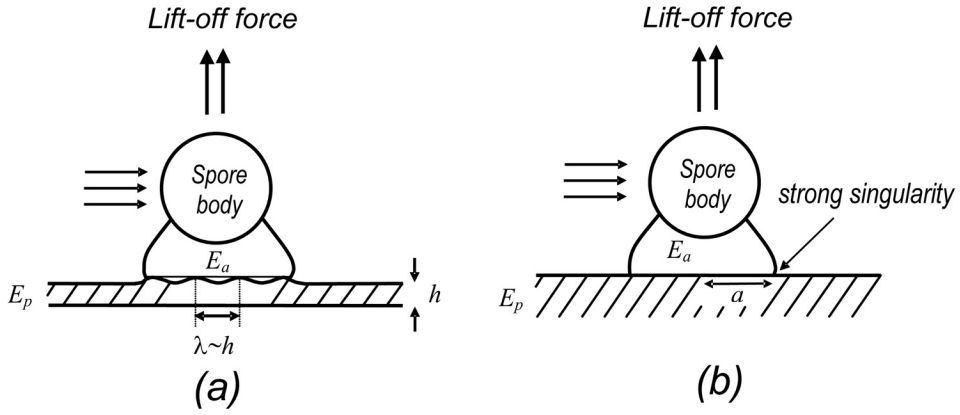

Figure 3. Schematic of adhesive release from PDMS coatings for relatively thick adhesive pads: (a) shows that cracks are produced inside the interface for thin PDMS films; (b) shows crack propagation from the edge for thick PDMS films.

external force. The crack length, in this case, is the wavelength (λ) of the instability, which is proportional to the thickness (h) of the PDMS film (Ghatak et al. 2000).

The pull-off stress (σ) then scales as:

$$\sigma \sim (WE_p/h)^{1/2} \tag{3}$$

where E_p is the elastic modulus of the polymer film. Equation 3 is similar to Kendall's Equation 1, except that the volume dilation of the film is not invoked. The entire process is controlled by elastic instability. The condition for the confinement of the PDMS film is that the ratio of the diameter of contact and film thickness be much larger than unity. However, as the *Ulva* spores do not satisfy the above condition, the pull-of force cannot be described by Equation 3, although it may apply to the case of the detachment for barnacles.

The second possibility is that the crack develops at the edge of the contact between the adhesive pad and the film (Figure 3b). This condition will be satisfied when the secreted adhesive is sufficiently thick and the adhesive subtends a significantly large angle of contact on PDMS. In that case the relevant length scale for the crack is the size of the contact zone.

The stress to delaminate the spore from the surface should be given by Equation 4:

$$\sigma \sim (WE_c/a)^{1/2} \tag{4}$$

where, E_c is the composite modulus of the adhesive and the PDMS film:

$$1/E_c = 1/E_a + 1/E_p \tag{5}$$

where E_p is the elastic modulus of the PDMS and E_a is the modulus of the spore adhesive pad (approximately 5 MPa within a few hours of release (Callow et al. 2000)). Equation 4 is essentially Kendall's Equation 2 with the modulus of the substratum replaced by the composite modulus. The composite modulus is used in Equation 5 since both the adhesive and the film can deform and store elastic energy. If $E_a < E_p$, the detachment force is controlled by the adhesive film and not by the PDMS film. Since the modulus of the stiffest PDMS coating in the present studies (9.4 MPa) was larger than that of the cured spore adhesive (5 MPa), and those of the other coatings were less than 5 MPa, a transition from 'adhesive-controlled release' to 'film-controlled release' may be expected. This point will be returned to later in the discussion.

A third situation can still arise, in which the spore adhesive pad is so thin and its angle on the PDMS surface is so small that the stress singularity at the edge of contact is very weak (Bogy, 1971). Since the crack cannot grow from the edge, the roles of either the pre-existing flaws or nucleation of cracks via instability need to be considered. In general, defects can nucleate at the adhesive/elastomer interface in the form of cavitation bubble just below the thickest part of the adhesive or at the locations indicated in Figure 4 (Jagota, personal communication) depending upon the dimension of the adhesive in comparison to the dimensions of the spore and the PDMS film. The size of these nucleated defects will then control the fracture stress.

Recent studies (Callow et al. personal observations) show that the adhesive secreted from *Ulva* spores spreads as a very thin film on hydrophilic surfaces, but not on hydrophobic surfaces. It is thus possible that the dominant mechanism of release of these spore adhesives from the PDMS coating is captured by Equation 4 (see Figure 3b). Based on Equation 4, the spore release behavior can be understood by examining how the quantity $E_c^{1/2}$ changes with respect to the modulus (E_p) of the PDMS coating. If it is assumed that the removal of

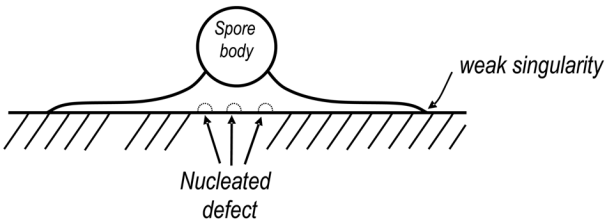

Figure 4. This figure illustrates the possible formation of crack at the interface for thin adhesive pads.

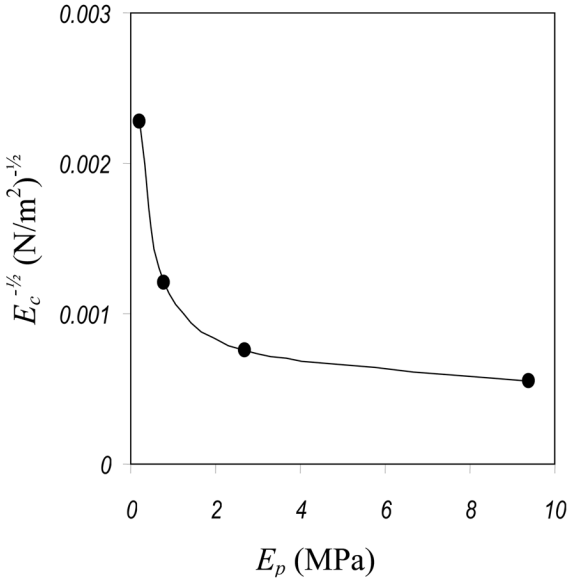

Figure 5. If the release behavior of spores from the PDMS films is inversely proportional to the pull-off stress σ, then it should scale with $E_c^{-1/2}$. Note the similarities between this prediction and the experimental data summarized in Figure 1.

the spore is inversely proportional to the pull-of stress σ, the removal efficiency should correlate with $E_c^{-1/2}$ (or $([E_a + E_p)/(E_a E_p)]^{1/2}$). Figure 5 shows such a plot, which resembles the experimental observations rather well.

The above analysis demonstrates that the release of zoospores should not depend on the thickness of the PDMS coating, which is consistent with the result that a six-fold increase in coating thickness from 16 to 100 μm had no significant influence on spore release. However, the data revealed an increase in spore removal at the greatest thickness of 430 μm. For such very thick coatings of relatively low modulus another effect may come into play. In a model experiment it was observed that thick PDMS films of low modulus are prone to elasto-hydrodynamic instability. If a cylindrical object remains adhered to such a film, and if this instability develops at the contact edge, the elastic waves penetrate through the interface causing an ultimate delamination of the object (see Figure 6). This model experiment suggests that the wavelength of elasto-hydrodynamic instability may give rise to another length scale of the crack penetrating through the interface.

Although, this problem of elasto-hydrodynamic instability remains to be worked out in detail, the wavelength of the associated instability is expected to be related to the thickness of the coating. Thus, the thickness of the coating may enter in the problem in way different from those underlying Equations 3 and 4, but it should apply only for very soft films.

The stronger influence of modulus on the detachment of sporelings may be related to the fact that in comparison to attached zoospores, the sporelings have a well-developed cellulosic cell wall that will contribute some rigidity to the system. This observation is also supported by data that reveal a positive relationship between sporeling age and the propensity for release from a commercial silicone elastomer (Schultz et al. 2003). Only 10% of 1 d old sporelings were released at a wall shear stress of 55 Pa compared to approximately 90% of 6 d old sporelings. The influence of coating thickness was also greater for the release of sporelings compared to spores. Ten-day-old sporelings grow in a dense 'forest' with individual rhizoids of 10–20 μm with frequent overlapping. These would represent a larger body with a larger surface area and the results would indicate that for sporelings, the critical coating thickness, and therefore the effective radius of the sporeling units, would be between 16 and 100 μm. Indeed, if this hypothesis was correct, the 20% of sporelings which remain on the thicker coats could be interpreted as those growing in smaller clumps and which were consequently more resistant to displacement. In this situation where the contact radius a is larger than the thickness of the film, i.e., the film is mechanically confined ($a \gg h$), it may be appropriate to use Equation 3.

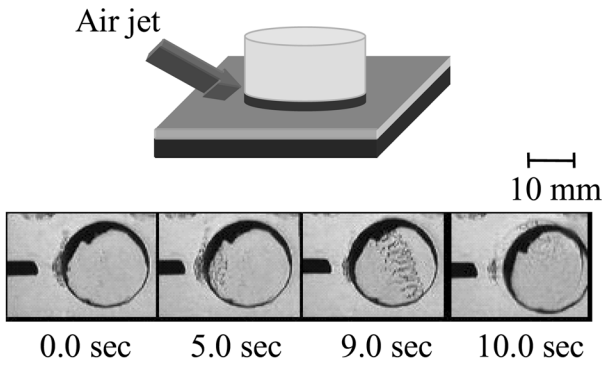

Figure 6. This model experiment shows that adherents can be removed from soft PDMS films by elastic waves on the surface. The cylindrical adherent is made of PDMS (5 mm thick) with a circular glass cover slip (18 mm diameter, 200 μm thick) bonded to it. When this cylinder is placed in contact with the PDMS film (0.3 MPa) with the glass side down, spontaneous adhesion results between the two. If an air jet (30 Pa pressure) is directed towards the PDMS film, an elastic wave is formed which propagates through the interface of the adherent and the film causing debonding of the two.

Acknowledgements

The Office of Naval Research are thanked for supporting this study under awards N00014-02-1-0521 to JAC & MEC and N00014-02-1-0518 to MKC.

References

Arce FT, Avci R, Beech IB, Cooksey KE, Wigglesworth-Cooksey B. 2003. Microelastic properties of minimally adhesive surfaces: A comparative study of RTV11^{TM} and Intersleek elastomers^{TM}. J Chem Phys 119:1671–1682.

Baier RE. 1973. Influence of the initial surface condition of materials on bioadhesion. Proc 3rd Int Congr Marine Corrosion and Fouling. Northwestern University Press, Evanston, Illinois, pp 633–639.

Becka A, Loeb G. 1984. Ease of removal of barnacles from various polymeric materials. Biotechnol Bioeng 26:1245–1251.

Berglin M, Lönn N, Gatenholm P. 2003. Coating modulus and barnacle bioadhesion. Biofouling 19 (Suppl):63–69.

Bogy DB. 1971. Two edge-bonded elastic wedges of different materials and wedge angles under surface tractions. J Appl Mech 38:377–386.

Brady RF, Singer IL. 2000. Mechanical factors favoring release from fouling release coatings. Biofouling 15:73–81.

Callow JA, Crawford SA, Higgins MJ, Mulvaney P, Wetherbee R. 2000. The application of atomic force microscopy to topographical studies and force measurements on the secreted adhesive of the green alga *Enteromorpha*. Planta 211:641–647.

Callow JA, Osborne MP, Callow ME, Baker F, Donald AM. 2003. Use of environmental scanning electron microscopy to image the spore adhesive of the marine alga *Enteromorpha* in its natural hydrated state. Colloids Surf B: Biointerfaces 27:315–521.

Callow ME. 1996. Ship-fouling: the problem and method of control. Biodeterioration Abstr 10:411–421.

Callow ME, Callow JA, Pickett-Heaps JD, Wetherbee R. 1997. Primary adhesion of *Enteromorpha* (Chlorophyta, Ulvales) propagules: quantitative settlement studies and video microscopy. J Phycol 33:938 – 947.

Callow ME, Jennings AR, Brennan AB, Seegert CE, Gibson A, Wilson L, Feinberg A, Baney R, Callow JA. 2002. Microtopographic cues for settlement of zoospores of the green fouling alga *Enteromorpha*. Biofouling 18:237 – 245.

Dexter SC. 1979. Influence of substratum critical surface tension on bacterial adhesion – *in situ* studies. J Colloid Interface Sci 70: 346 – 354.

Finlay JA, Callow ME, Ista LK, Lopez GP, Callow JA. 2002a. The influence of surface wettability on the adhesion strength of settled spores of the green alga *Enteromorpha* and the diatom *Amphora*. Integ Compar Biol 42:1116 – 1115.

Finlay JA, Callow ME, Schultz MP, Swain GW, Callow JA. 2002b. Adhesion strength of settled spores of the green alga *Enteromorpha*. Biofouling 18:251 – 256.

Fowler J, Cohen L. 1994. Practical statistics for field biology. Chichester: John Wiley and Sons.

Ghatak A, Shenoy V, Chaudhury MK, Sharma A. 2000. Meniscus instability in thin elastic film. Phys Rev Lett 85:4329 – 4332.

Gray NL, Banta WC, Loeb GI. 2002. Aquatic biofouling larvae respond to differences in the mechanical properties of the surfaces on which they settle. Biofouling 18:269 – 273.

Hayden HS, Blomster J, Maggs CA, Silva PC, Stanhope MJ, Walland RJ. 2003. Linnaeus was right all along: *Ulva* and *Enteromorpha* are not distinct genera. J Phycol 38:277 – 294.

Hoipkemeier-Wilson L, Schumacher JF, Carman ML, Gibson AL, Feinberg AW, Callow ME, Finlay J A, Callow JA, Brennan AB. 2004. Antifouling potential of lubricious, micro-engineered, PDMS elastomers against zoospores of the green fouling alga *Ulva* (*Enteromorpha*). Biofouling 20:53 – 63.

Jeffrey SW, Humphrey GF. 1975. New spectrophotometric equations for determining chlorophylls a, b, c1 and c2 in higher plants, algae and natural phytoplankton. Biochem Physiol Pflanz 167:191 – 194.

Kavanagh CJ, Schultz MP, Swain GW, Stein J, Truby K, Darkangelo-Wood C. 2001. Variation in adhesion strength of *Balanus eburneus*, *Crassostrea virginica* and *Hydroides dianthus* to fouling-release coatings. Biofouling 17:155 – 167.

Kendall K. 1971. The adhesion and surface energy of elastic solids. J Phys D: Appl Phys 4:1186 – 1195.

Kohl JG, Singer IL. 1999. Pull-off behavior of epoxy bonded to silicone duplex coatings. Prog Org Coat 36:15 – 20.

Newby B-M, Chaudhury MK. 1997. Effect of interfacial slippage on viscoelastic adhesion. Langmuir 13:1805 – 1809.

Schultz MP, Finlay JA, Callow ME, Callow JA. 2000. A turbulent channel flow apparatus for the determination of the adhesion strength of microfouling organisms. Biofouling 15:243 – 251.

Schultz MP, Finlay JA, Callow ME, Callow JA. 2003. Three models to relate detachment of low form fouling at laboratory and ship scale. Biofouling 19 (Suppl):17 – 26.

Shoaf TW, Lium BS. 1976. Improved extraction of chlorophyll a and b from algae using dimethyl sulfoxide. Limnol Oceanogr 21:926 – 928.

Singer IL, Kohl JG, Patterson M. 2000. Mechanical aspects of silicone coatings for hard foulant control. Biofouling 16:301 – 309.

Starr RC, Zeikus JA. 1987. The culture collection at the University of Texas. J Phycol 23 (Suppl):S1 – S27

Stein J, Truby K, Darkangelo-Wood C, Takemori M, Vallance M, Swain G, Kavanagh C, Kovach B, Schultz M, Wiebe D, Holm E, Montemarano J, Wendt D, Smith C, Meyer A. 2003. Structure-property relationships of silicone biofouling-release coatings: effect of silicone network architecture on pseudobarnacle attachment strengths. Biofouling 19:87 – 94.

Sun Y, Akhremitchev B, Walker GC. 2004a. Using the adhesive interaction between atomic force microscopy tips and polymer surfaces to measure the elastic modulus of compliant samples. Langmuir 20:5837 – 5845.

Sun Y, Guo S, Kavanagh CJ, Swain GW. 2004b. Surface elastic modulus of barnacle adhesive and release characteristics from silicone surfaces. Biofouling 20: 279 – 289.

Swain GE. 1999. Redefining antifouling coatings. Paint Coatings Europe July 1999: 18 – 25.

Swain GW, Schultz MP. 1996. The testing and evaluation of nontoxic antifouling coatings. Biofouling 10:187 – 197.

Townsin RL. 2003. The ship hull fouling penalty. Biofouling 19 (Suppl):9 – 15.

Vorvolakos K, Chaudhury MK. 2003. The effects of molecular weight and temperature on the kinetic friction of silicone rubbers. Langmuir 19:6778 – 6787.

Wynne KJ, Swain GW, Fox RB, Bullock S, Ulik J. 2000. Two silicone nontoxic fouling release coatings: hydrosilation-cured PDMS and $CaCO_3$-filled, ethoxysiloxane cured RTV11. Biofouling 16:277 – 288.