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# Investigation of the biofouling properties of several algae on different textured chemical modified silicone surfaces

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ABSTRACT

Engineered pillars, pits and grooves spaced 3, 6, 9 and 12 μm apart were fabricated on siloxane modified acrylic resin films. The effect of feature size, geometry, and wettability on the settlement of different algae was evaluated. These films showed various antifouling performances to *Ulothrix*, *Closterium* and *Navicula*. For *Navicula* (length: 10–12 μm), the feature size and geometry displayed a substantial correlation with the antifouling properties. The film with pillars spaced 3 μm reduced *Navicula* settlement by 73% compared to the control surface. For *Closterium* (length: 45–55 μm), their responses were governed by the same underlying thermodynamic principles as wettability, the largest reduction in *Closterium*, 81%, was obtained on the surface with grooves spaced 12 μm apart. For *Ulothrix* (length: 5–8 mm), the surface also showed the best antifouling performance, the reduction ratio of the settlement on the surface with grooves spaced 12 μm apart could even reach 92%. At last, physical fouling deterrent mechanisms for the films with various textures were analyzed in detail. The feature size and geometry display a substantial correlation with the antifouling properties when the size of fouling algae is close to the textures. With the increasing size for algae, antifouling performance was getting better on surface with pillars or grooves because the algae are bridged between two or more features other than stabilizing its entire mass on one single feature or able to settle between features.

## 1. Introduction

Biofouling is generally defined as the accumulation of living organisms including microorganisms, algae and animals on a surface immersed in seawater. This undesirable colonization has serious impacts that can be environmental, economic, or ecological-related [1–3]. Biofouling is of great concern in numerous applications ranging from biosensors to industrial and marine equipment. The self-polishing coatings are effective on reducing biofouling because of slow release of tin, copper or other toxins in time [4–6]. But they had detrimental impact on nature [7–9]. In order to protect our nature, the development of non-toxic and environment-friendly anti-fouling paints is the main trend of marine antifouling coatings. The ideal coating should be also with antifouling and foul releasing properties.

Poly(dimethysiloxane) (PDMS) or silicone materials have demonstrated good fouling-release (FR) performance under suitable hydrodynamic conditions, and they are considered non-toxic marine coatings [10–13]. But, PDMS has some obvious drawbacks, such as poor adhesion with substrate, low mechanical strength and high cost. The siloxane modified acrylic resin (SMAR), also has good fouling-release (FR) performance, and its mechanical properties are better than silicone [14]. But, the SMAR is not inherently antifouling like other low surface energy antifouling paints. Biofouling will occur under low flow conditions.

Shark, mollusk shells and other marine animals show excellent antifouling performance on their skins because their surfaces display special micro/nano binary textures. Inspired by the interesting phenomena, the materials with micro/nano-textures on the surface might also demonstrate the excellent anti-fouling performance. Carman et al. presented a biomimetically inspired surface topography (Sharklet AFTM), which had feature dimensions smaller than the spore body, significantly reduced settlement density by 86% relative to smooth PDMS [15]. And they suggested that spores' responses were governed by the same underlying thermodynamic

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principles as wettability. Results from Schumacher indicated that engineered microtopographies reduced *Ulva* spores settlement by up to 58% (diameter circular pillars and 10 μm equilateral triangles) and by 77% for microtopographies replicating shark skin [16]. An indirect correlation between spore settlement and a newly described engineered roughness index was identified in this research.

Previous results evaluated the effect of topographic feature size, geometry, wettability and roughness on settlement of *Ulva* zoospores, but it was necessary to address algae size in relation of attachment. All of these factors were important for the anti-fouling properties. Static bioassays were conducted on microtextured polyimide surfaces using four diatom species, *Fallaciacarpentariae*, *Nitzschia cf. paleacea*, *Amphora* sp. and *Navicula jeffreyi* with cell sizes ranging from 1–14 μm. Their work directly tested attachment 'point theory' and preliminarily revealed the effect of cell sizes on anti-fouling properties [17]. To the best of our knowledge, the relationship between algae size and texture geometry have not been reported in detail until now.

In this paper, taking advantage of low surface energy and surface textures, SMAR films with various textures are prepared. Three kinds of common algae including *Ulothrix*, *Closterium* and *Navicula* are used to evaluate the biofouling resistance properties of as-prepared samples. Systematic investigation of surface topography, wet/dewettability, anti-fouling performances are performed by corresponding equipments. The anti-fouling mechanisms of textured coatings are analyzed based on the three key factors including of surface wettability, morphology (feature size and spacing), and algae size.

## 2. Experimental

### 2.1. Materials

The polydimethylsiloxane (PDMS) elastomer (SILASTIC DC-184, Dow Corning Corporation) was used as the masterplate material for texture formation due to its high reproducibility and good elasticity. The elastomer was prepared by hand mixing ten parts by weight of PDMS prepolymer with one part by weight of curing agent. The mixture was degassed at ambient temperature for 90 min, then typically cured at 70 °C for 12 h.

The base material for topographical modification used in this study was siloxane modified acrylic resin (SMAR) (SKD002, Shanghai Chaoyu Corporation). Six parts of SMAR and two parts of hexamethylene diisocyanate trimer (CORONATE HX, NPU Corporation) were dissolved in three parts of xylene by weight. The mixture was degassed for 30 min and allowed to be cured at 70 °C for 12 h.

### 2.2. Surfaces

The method used to fabricate various surface textures is simple and reproducible. The schematic process flow to create pillars, pits and groove with different area density was shown in Fig. 1. The texture was initially etched in silicon wafers using the inductively coupled plasma etching process as previously described by McAuley [18]. The above PDMS mixture was degassed at room temperature for about 1.5 h to remove any air bubbles in the mixture. The PDMS mixture was spin-coated on the wafers, then heat treated at 70 °C for 12 h in a vacuum oven. Negative texture was replicated directly from the etched wafer. The PDMS elastomer with negative texture was used to produce a positive replica in SMAR. At last, the above SMAR mixture was degassed at room temperature for about 0.5 h to remove bubbles. The SMAR mixture was spin-coated on the textured PDMS elastomer, after being heat treated at 70 °C for 12 h, the positive textures were transferred to SMAR from the negative textures.

Surface textures included circular pillars, continuous grooves, and circular pits. Their diameter or width was 3 μm. Pillars, pits and grooves were spaced 3, 6, 9 and 12 μm apart (Fig. 2). Control surfaces were uniformly smooth.

### 2.3. Contact angle measurements

The static water contact angles of the free-standing SMAR films with textures were measured according to the sessile droplet method using a drop shape analysis system (Data Physics OCA20, Germany) with a computer-controlled liquid dispensing system. Deionized water droplet with a volume of 4 μL was employed as the source for the measurements. The contact angle was the average of three replicates for each textured sample, and each sample's contact angle was tested three times.

### 2.4. Algae settlement assay

SMAR samples containing 3 μm diameter circular pillars, pits and 3 μm width continuous grooves, spaced 3, 6, 9 and 12 μm apart were evaluated for settlement of algae. Three replicates of each textured type were tested as films pasted on glass slides (size: 76 mm × 25 mm). A uniformly smooth SMAR film was used in the assay and served as a control for direct comparison.

The three algae species used, *Ulothrix*, *Closterium* and *Navicula* were all harvested from the East China Sea. The length of *Ulothrix*, *Closterium* and *Navicula* was, in order, 5–8 mm, 45–55 μm and 10–12 μm, respectively; the width of three algae species was all 3–4 μm. Growth conditions for all algae were 12:12 h light:dark cycle at 25 °C. *Closterium* and *Navicula* were supplemented with Guillard's F/2 medium, *Ulothrix* was supplemented with Selenite Enrichment (SE) medium.

The glass slides with films were placed on sample holder which was immersed in the bottom of the beaker filled with 15 mL filtered seawater and 15 mL of algae culture suspension. The density of the *Closterium* and *Navicula* culture suspension was $1\text{–}3 \times 10^6$ cells $\text{mL}^{-1}$. The chlorophyll value of *Ulothrix* culture suspension was 1.5547 ($\mu\text{g cm}^{-2}$).

Then, the algae were left to be settled for 7 days. The films after algae settlement were rinsed by dipping in a new beaker of filtered seawater three times to remove unattached algae.

The films settled by *Closterium* and *Navicula* were fixed with 2% glutaraldehyde in artificial seawater as described by Callow [19]. *Closterium* and *Navicula* counts were quantified using a Dimension 3100v Laser Scanning Confocal Microscope (LSCM) analysis system. Ten images and counts were obtained from 10 random fields of view per 0.64 $\text{mm}^2$ area for *Closterium* and 0.16 $\text{mm}^2$ area for *Navicula*. The settlement of *Ulothrix* on the films was determined by chlorophyll values by using a Lambda 950 UV/Vis/NIR Spectrophotometer.

Every textured film's antifouling property was evaluated by the reduction ratio ($R_r$) of algae density compared to the control film.

$$R_r = \frac{(D_c - D_n)}{D_c} \tag{1}$$

$D_n$, the algae density of the textured film; $D_c$, the algae density of the control film; when the algae density of textured film was higher than control surface, the $R_r$ then was a negative value.

## 3. Results and discussion

Understanding the role of surface textures in deterring different organisms is important in terms of optimizing the performance of coatings designed to prevent or reduce biofouling. The SMAR