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Antimicrobial Behavior of Novel Surfaces Generated by Electrophoretic Deposition and Breakdown Anodization

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Antimicrobial Behavior of Novel Surfaces Generated by Electrophoretic Deposition and Breakdown Anodization

A Thesis submitted in partial satisfaction of the requirements for the degree of

Master of Science

in

Microbiology

by

Jessamine Quijano Flores

December 2013

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Acknowledgments

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My sincere appreciation goes to Dr. Richard Cardullo for being supportive and an amazing coordinator for my Fellowship Bridge to the Doctorate that was supported by the National Science Foundation (NSF).
Dedication

I dedicate this to my family and friends whom have supported me in this incredible journey. This achievement could not have been made without my parents struggle to give their children a fighting chance in succeeding in life by relocating to the United States. My parent’s prayers without a doubt have allowed me to reach this amount of accomplishment and I thank them sincerely for this. My husband Ruben has been a pillar in holding me up in times of hardship, which has allowed me to triumph. My friends Diana Villa and Cynthia Guevara were of great emotional support in my educational journey.
ABSTRACT OF THE THESIS

Antimicrobial Behavior of Novel Surfaces Generated by Electrophoretic Deposition and Breakdown Anodization

by

Jessamine Quijano Flores

Master of Science, Graduate Program Microbiology
University of California, Riverside, December 2013
Sharon L. Walker, Chairperson

Managing biofouling is a critical aspect in a wide range of industries and addressing this concern is of optimal interest. In this study, the mass transfer of a model marine bacterium (*Halomonas pacifica* g) was investigated on engineered surfaces ranging from superhydrophobic to superhydrophilic. The quantification of the deposition kinetics was achieved using a specially designed parallel plate flow chamber system under a range of relevant solution chemistries on the test surfaces. *Halomonas pacifica* g was further characterized to determine its zeta potential and hydrophobicity. Test surfaces were generated via breakdown anodization or electrophoretic deposition, and properties including surface roughness, contact angle, and capillary diffusivity were quantified. The greatest deposition was observed on of the superhydrophilic surface, which had micro- and nano- scale hierarchical structures composed of titanium oxide on a titanium plate. Conversely, one of the hydrophobic surfaces with micro-porous films overlaid with polydimethylsiloxane appeared to be most resistant to cell attachment.
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Table 2 The surface structures were characterized by a profilometer, and wetting properties were measured in terms of static contact angle, roll-off angle, and hydraulic diffusivity. Zeta potential was also measured at 10mM IS. Based on the contact angles, the prepared surfaces were classified as superhydrophobic (Samples TiO2-B-10°C, TiO2-B-25°C, TiO2-BE), superhydrophilic (Samples SiO2-E, SiO2-BE-25°C, SiO2-BE-75°C), and hydrophobic (Samples PDMS-B, PDMS-E). 16
1. **Introduction**

Biofouling is problematic for a variety of industries including cosmetics, pharmaceuticals, medical devices, and global marine industries [1-3] leading to staggering costs. As of 2010, it was estimated that the annual cost due to hull fouling for current U.S. Navy ships and infrastructure ranged from $180-250 million [4]. Those costs are directly related to cleaning and coating costs, as well as frictional drag that increases fuel consumption. The fouling process on marine surfaces begins with bacterial colonization and biofilms, followed by other microorganisms such as unicellular algae (i.e. diatoms) and eventually invertebrates such as soft corals, sponges, barnacles, and mussels [5]. The approach to combat biofouling may differ by industry although the underlying challenge is the same for all, which is in the inhibition of the initial stages of bacterial attachment to prevent microbial biofilms [6].

The ever-present battle to inhibit fouling on ships has been addressed as early as the 1500s, with the use of copper plates on wooden ship hulls to decrease fouling [2, 7]. By the 1960’s antifouling paints, which contain biocide materials such as copper and tributyltin (TBT) became commonplace for the prevention of cell adherence due to the leaching of these materials. However, it was discovered that the corrosion process of copper lead to the release of cuprous oxide that interfere with cell division and that the copper and TBT were toxic to marine organisms [8, 9]. This led to the International Maritime Organization to ban TBT in 2001 due to its high toxicity and long half-life of 3 months [10]. Copper having lower toxicity level is currently under review by the US EPA for future restrictions, with the final outcome of that review anticipated in 2015 [11, 12].
There are three principal approaches to combat biofouling: the first employs the direct use of biocides as shown prior, the second is mechanical detachment, and the third is surface modification to prevent cell adherence. Antibiotics and cleaning chemicals are other biocides that are used to kill and degrade biofilms [13]. The medical community has attempted to load antibiotics onto medical devices to prevent infections and a recent study demonstrated a novel coating that slowly released antibiotics as a potential strategy to prevent specific microbial adherence [14]. Cleaning chemicals are used to degrade biofilms in dental unit waterlines to prevent patients and staff from exposure to these microorganisms [15]. The second principal approach once again is mechanically detaching attached microorganisms, but it has been shown that mechanical detaching fouling from ship hull has high maintenance concerns compared to other methods [16].

The final principal approach has been accomplished by the efforts of the material science community to explore novel surface modification techniques in an effort to develop anti-microbial, non-toxic surfaces through chemical and or structural modification [17-24]. Examples of such treatments include coating with self-assembled monolayers (SAMs), which can have finely tuned chemical properties: wettability, controlled functional groups, or charge density [21, 23, 24]. SAMs with ω-substituted alkane thiolates on gold, have been reported to have a positive correlation with spore attachment with increased surface hydrophobicity [17]. Many chemical coatings which incorporate such effective functional groups within polymeric materials have been investigated such as siloxane urethane, poly(ethylene glycol) polymers and combinations of various materials such as patterned poly(ethylene glycol) and fluorinated surfaces [19].
The production of fluorinated polymers that create hydrophobic surfaces were also found to be effective in generating surfaces that cells could be released from with sufficient shear force (i.e., ship movement or rinsing) [20]. Furthermore, aminoproply terminated poly(dimethyl siloxane) (PDMS) macromers prepared by a single amine group anchoring the PDMS were fabricated and shown to reduce biofilm retention. This was attributed to the hydrophobic nature of these surfaces, and it is thought that these types of materials can be further improved for antimicrobial properties [22]. Previously, it was also reported that zeolite-coated aluminum alloy and stainless steel surfaces had less bacterial cell deposition as compared to uncoated, bare metal surfaces [18].

There are a broad range of factors that are reported in playing a role in cell attachment including wettability/hydrophobicity, surface chemistry, surface roughness and topography, surface elastic modulus and color [17, 20, 25-29]. Wettability has been shown to be of great importance in both field and laboratory assays and thus a factor that must be addressed when developing antifouling surfaces [17, 25]. Surface roughness and topography is indeed a feature that must be considered when engineering surfaces since it has been shown to alter attachment of bacteria [26, 27]. Elastic modulus of the surfaces have also been proven to be key in addressing bioadhesion and must be contemplated in selecting antifouling surfaces [28]. Color has been shown to have an impact on fouling behavior, higher densities of species were found to favor black colored surfaces rather than white in different surface materials [29-31].

This study was aimed to investigate the attachment of a model marine organism to novel surfaces created by a hybrid method of employing breakdown anodization (BDA)
and electrophoretic deposition (EPD) [33] and to evaluate the surface treatments’ ability to control cell adhesion. Upon obtaining the model surfaces, which ranged from superhydrophilic to superhydrophobic with different surface morphologies and surface hydrophobicities, they were characterized in terms of hydrophobicity, surface roughness, and zeta-potential. This characterization was followed up with extensive experimentation to evaluate these surfaces’ ability to minimize or maximize the quantification of bacterial mass transfer rates.

2. Material and Methods

2.1 Bacterial Cell Preparation

The model marine bacterium selected for this study, *Halomonas pacifica* (ATCC 27122), was previously obtained from the ATCC (American Type Culture Collection, Rockville, MD) due to its fouling properties [34]. This bacterium was labeled with enhanced green fluorescent protein (EGFP) and gentamicin resistance via electroporation for visualization and is referred to as *H. pacifica g* [35]. *H. pacifica g* is a non-motile rod-shaped gram-negative bacterium and is grown at 30 °C in artificial seawater composed of sea salts (38.5 g/L, Sigma-Aldrich, Buchs SG, Switzerland), bacteriological peptone (5 g/L, Sigma), and yeast extract (1 g/L, Sigma) with gentamycin sulfate antibiotic (30 mg/L, OmniPur, Gibbstown, NJ) [36]. Pre-cultures made from marine agar plates (55.1 g/L, BD Diagnostic Systems) were used to inoculate second cultures and grown for 16 hours for further deposition and characterization studies [37]. Harvesting of cells was done by centrifugation (accuSpin 3R centrifuge, Fisher Scientific, Pittsburgh,
PA) for 15 minutes at 3689 g and further rinsing the pelleted cells twice with 10 mM KCl. The KCl solution was prepared with reagent-grade salt (laboratory grade, Fisher Sci.) and deionized (DI) Water (Millipore, Billerica, MA) at an unadjusted pH (5.6-5.8).

### 2.2 Bacterial Surface Characterization

To analyze the relative hydrophobicity of *H. pacifica* g cells, a semi-quantitative microbial adhesion to hydrocarbons (MATH) test was employed [38]. The relative hydrophobicity of the organism in each of these solutions is reported at the percent of total cells that partition into the model hydrocarbon (dodecane) [39]. Specifically, test tubes were set up to have 4 mL of the cell suspension with 1 mL of n-dodecane (laboratory grade, Fisher Sci.). Test tubes were vortexed (AutoTouch Mixer Model 231, Fisher Sci.) for 2 minutes followed by a rest period of 15 minutes to allow phase separation and the final absorbance reading after the rest period was compared to the initial absorbance acquired after harvesting. The optical density of the cells in the aqueous phase was measured using a spectrophotometer at 546 nm (BioSpec-mini, Shimadzu Corp., Kyoto, Japan). A second solution condition (ionic strength (IS) = 100mM KCl) was also test to compliment conditions set up for deposition studies. *H. pacifica* g cells were harvested and a suspension of cells was prepared to have an optical density of 0.2-0.25 in 10 mM KCl at 546 nm. Ionic strengths of 10 mM and 100 mM have been shown to correspond to freshwater and 5% seawater [40].

Determination of the zeta potential of the bacterial cells was conducted using a ZetaPALS analyzer (Brookhaven Instruments Corp., Holtsville, NY) at 25 °C with
harvested cells suspended in 10 mM and 100 mM KCl solution. This test was repeated at least three times with freshly harvested cells and the measured electrophoretic mobility values were converted to zeta potential using the Smoluchowski equation [41].

2.3 Material Surface Preparations and Characterization

Quartz slides have previously been used to observe deposition behavior under electrostatically unfavorable [42] and favorable conditions [35] (when coated with positively charged amininosilane). In this study, unmodified quartz microscope slides (electron microscopy Diatome quartz microscope slide, 3”×1”, Fisher Sci.) cut to fit (9×20 mm) within the flow chamber. Prior to the deposition experiments on to the quartz, samples were cleaned by submerging and sonicated in 2% Extran® solution (EMD chemicals Inc., Darmstadt, Germany) and for 15 minutes at room temperature, followed by a thorough rinse with deionized (DI) water. Next, the quartz samples were submerged in 2% RBS 35 detergent solution (Pierce Biotechnology, Rockford, IL) and sonicated for 15 minutes at 50 °C, followed by a DI water rinse. Finally, quartz samples were submerged in Nochromix (Godax Laboratories, Inc., Cabin John, MD) solution overnight and rinsed with DI water the following day and allowed to air dry prior to use in transport studies.

The novel surfaces tested were created by electrophoretic deposition (EPD) and breakdown anodization (BDA) to produce nano- and micro-porous surfaces [32, 33, 43, 44]. Figure 1 shows a schematic illustration of BDA and EPD methods used to develop varying surface structures. In the BDA method, titanium (Ti) plates (ultra-corrosion-
resistant titanium grade 2, 0.020" thick, McMaster, Santa Fe Springs, CA) were used as anode and cathode electrodes that were submerged in an electrolyte solution (DI water, pH = 3 adjusted using nitric acid, 70 % ACS reagent, Sigma-Aldrich). An electric potential of 120 V was applied to the titanium electrodes for 30 min during the anodization process. The solution temperature was maintained using circulating water.

![Fabrication processes for micro/nano hierarchically structured surfaces. For micro-porous structures, breakdown anodization (BDA) is used with different electrolyte temperatures. For nano porous structures, electrophoretic deposition (EPD) is used with different nanoparticles. The hierachical micro- and nano-porous structures are produced by a series of BDA and EPD. The electrolyte temperature and the nanoparticles affect the surface morphology and the surface energy, respectively.](image)

Figure 1. Fabrication processes for micro/nano hierarchically structured surfaces. For micro-porous structures, breakdown anodization (BDA) is used with different electrolyte temperatures. For nano porous structures, electrophoretic deposition (EPD) is used with different nanoparticles. The hierachical micro- and nano-porous structures are produced by a series of BDA and EPD. The electrolyte temperature and the nanoparticles affect the surface morphology and the surface energy, respectively.

(Polystate, Cole-Parmer, Vernon Hills, IL) surrounding the BDA cell since micro-structures are strongly influenced by the temperature [32]. The resulting titanium dioxide (TiO₂) surfaces generated by only BDA are referred to as TiO₂-B-10°C and TiO₂-B-25°C (B signifies BDA, last digits signifies temperature in degree Celsius) unless otherwise stated the materials were generated at a temperature of 24 °C.
EPD was used to produce nanostructure surfaces by depositing both hydrophobic silicon dioxide (SiO$_2$) nanoparticles coated with poly(dimethyl siloxane) (PDMS) and hydrophilic TiO$_2$ nanoparticles onto unmodified titanium plates. Noting that silicon dioxide (SiO$_2$) nanoparticles coated with (PDMS) will be referred to just (P)SiO$_2$ for the remainder of this paper. (P)SiO$_2$ nanoparticles (14 nm, PlasmaChem, Berlin, Germany) were dispersed (1 g/L) in a mixture of 90 vol.% methanol (ACS Reagent, Baker analyzed) and 10 vol.% DI water. The resulting sample generated by EPD with (P)SiO$_2$ is referred to as (P)SiO$_2$-E (E indicates EPD). TiO$_2$ nanoparticles (20 nm, anatase, Sigma-Aldrich) were dispersed in acetic acid to achieve 1 g/L TiO$_2$ suspensions. An electric field of 30 or 60 V/cm was subjected to the electrodes for varying times, specifics found on Table 1. The suspension temperature was maintained constant at 24°C, to deposit nanoparticles onto the substrate.

For hierarchical micro- and nano-structured surfaces, BDA was conducted on titanium plates to make micro-porous layers followed by EPD of nanoparticles (either TiO$_2$ or (P)SiO$_2$) onto the micro-porous layers as described above. The resulting samples from the combination of BDA and EPD are referred to as TiO$_2$-BE, (P)SiO$_2$-BE-25°C, and (P)SiO$_2$-BE-75°C (BE indicates the combination BDA and EPA, last digits signifies temperature in degree Celsius). In EPD, temperature was maintained constant at 24°C.

The patterned BDA and EPD surfaces were further coated with PDMA such that specific levels of hydrophobicity and surface roughness could be generated. PDMS was coated on the surfaces by spin-coating at 3000 rpm for 1 min. The resulting samples are stated as PDMS-B or PDMS-E. These eight samples (TiO$_2$-B-10°C, TiO$_2$-B-25°C, TiO$_2$-
BE, (P)SiO$_2$-E, (P)SiO$_2$-BE-25°C, (P)SiO$_2$-BE-75°C, PDMS-B, and PDMS-E), which have different morphologies and surface hydrophobicities, were positioned in the parallel plate flow cell and utilized for the bacterial deposition experiments. Table 1 summarizes the fabrication methods and materials used to produce the novel test surfaces with their surface characteristics in terms of surface roughness (Ra), static contact angle, roll-off angle, hydraulic diffusivity, and surface zeta-potential.

The morphology of the prepared surfaces was observed with a scanning electron microscope (SEM, JEOL 6320FV Field-Emission High-resolution SEM and Zeiss, He-Ion microscopy). Surface roughness was measured by a profilometer (tencor P-16 surface profilometer (TM) Milpitas, CA) at five distinct points on each sample. The area scanned was $2 \times 4 \text{ cm}^2$ and the average root mean square (RMS) surface roughness was calculated using commercial software provided by the profilometer manufacturer. Static contact angles were measured by a goniometer (Kyowa, DM-CE1, Saitama, Japan). Averaged contact angles were obtained from the measurements at four different points on each sample. Static contact angles were calculated using the tangential curvefitting method. From the advancing and receding contact angles, the roll-off angles were calculated [45]. The capillary rise measurement (CRM) has been used to characterize water transport speed in terms of hydraulic diffusivity [46].
Table 1. Fabrication methods and conditions to produce different surface structures and energies. Breakdown anodization (BDA) and electrophoretic deposition (EPD) were used for micro and nano surface structures. Different electrolyte temperatures and different nanoparticles were used to change the surface structures and energies in BDA and EPD, respectively. To change surface energy, polydimethylsiloxane (PDMS) was spin-coated on the micro- and nano-structured surface.

<table>
<thead>
<tr>
<th>Name</th>
<th>Fabrication method</th>
<th>BDA condition (potential, time, electrolyte temperature)</th>
<th>Particles for EPD (material, size)</th>
<th>EPD condition (potential, time)</th>
<th>Spin coating (material, rotating-speed, time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂-B-10°C</td>
<td>BDA</td>
<td>120 V, 30 min, 10 °C</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TiO₂-B-25°C</td>
<td>BDA</td>
<td>120 V, 30 min, 25 °C</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TiO₂-BE</td>
<td>BDA + EPD</td>
<td>120 V, 30 min, 10 °C</td>
<td>TiO₂, 20 nm</td>
<td>30 V, 2 min</td>
<td>N/A</td>
</tr>
<tr>
<td>(P)SiO₂-E</td>
<td>EPD</td>
<td>N/A</td>
<td>Hydrophobic SiO₂, 14 nm</td>
<td>60 V, 20 min</td>
<td>N/A</td>
</tr>
<tr>
<td>(P)SiO₂-BE-25°C</td>
<td>BDA + EPD</td>
<td>120 V, 30 min, 25 °C</td>
<td>Hydrophobic SiO₂, 14 nm</td>
<td>60 V, 10 min</td>
<td>N/A</td>
</tr>
<tr>
<td>(P)SiO₂-BE-75°C</td>
<td>BDA + EPD</td>
<td>120 V, 30 min, 75 °C</td>
<td>Hydrophobic SiO₂, 14 nm</td>
<td>60 V, 10 min</td>
<td>N/A</td>
</tr>
<tr>
<td>PDMS-B</td>
<td>BDA + PDMS</td>
<td>120 V, 30 min, 25 °C</td>
<td>N/A</td>
<td>N/A</td>
<td>PDMS, 3000 rpm, 1 min</td>
</tr>
<tr>
<td>PDMS-E</td>
<td>EPD + PDMS</td>
<td>N/A</td>
<td>TiO₂, 20 nm</td>
<td>30 V, 1.5 min</td>
<td>PDMS, 3000 rpm, 1 min</td>
</tr>
</tbody>
</table>
Surface zeta potential values were obtained using a clamping cell attached to a commercial streaming potential analyzer (Electro Kinetic Analyzer (EKA), Brookhaven Instruments, Holtsville, NY). The engineered samples were placed in the cell flat against a 10 mm piece of grooved poly(methylmethacrylate) (PMMA) spacer, further described elsewhere [47]. Test solutions of 10 mM or 100 mM KCl were introduced into the rectangular channels of the PMMA spacer by the inlet/outlet tubing connected to Ag/AgCl electrodes. First, a sample coupon was loaded into the clamping cell and rinsed with DI water. Then, the zeta potential was characterized with DI water, 5 mM KCl, and 10 mM KCl as background solutions separately. All the measurements were performed at room temperature (23 °C) without adjusting pH.

2.4 Bacterial Deposition Studies

*H. pacifica* g deposition experiments employed a modified parallel plate flow chamber (PP) [48, 49] (product 31-010, GlycoTech, Rockville, MA) positioned on the stage of an upright fluorescent microscope (BX-52, Olympus). The inner dimension of the chamber are 6 cm×1 cm×0.0762 cm and is composed of a Plexiglas block that is mounted by a flexible silicon elastomer gasket and a microscope slide that vacuum grease seals all together. The flow deck has a groove (9 × 20 mm) where samples are held in place by vacuum grease. The fluid stream enters the chamber from a capillary tube that is connected to a syringe being pressed by a peristaltic pump at a flow rate of 0.1 mL/min, corresponding to an average flow velocity of 0.79 m/h, and a Péclet number of 6.47×10⁻⁴ [50]. The fluorescently labeled bacteria are imaged by a 40× long working
distance objective (UPlanFl, Olympus) using a filter at excitation and emission wavelengths of 480 nm and 510 nm, respectively (Chroma Technology Corp., Brattleboro, VT).

Deposition of \textit{H. pacifica} cells was observed over a 30 minute period with images recorded with a digital camera (Demo Retiga EXI Monochrome, QImaging) every minute to determine the kinetics of deposition cells for each time interval. Enumeration of cells was determined by comparison of successive images. A suspension of cells ($1 \times 10^8$ cells/mL) was utilized and the concentration was determined with a counting chamber (Bürker-Türk chamber, Marienfield Labora- tory Glassware, Lauda-Königshofen, Germany). Deposition experiments were conducted at 10 and 100 mM KCl with unadjusted pH (5.6-5.8) at ambient temperature (22-25 °C). Engineered surfaces prepared by the techniques describe above were rinsed with DI water within the parallel plate flow cell prior to deposition experiments.

The number of bacterial cells deposited versus time was plotted and calculation of bacterial deposition flux ($J$) was achieved by dividing the initial slope of the line by the microscope viewing area (230 µm × 170 µm). The mass transfer rate coefficient for the bacteria, $k_{pp}$, is calculated using the bacterial deposition flux ($J$) and the bulk cell concentration, $C_0$, via [18, 41, 51]:

$$k_{pp} = \frac{J}{C_0}$$

(1)

Deposition experiments were conducted under chemically “unfavorable” conditions on quartz for the sake of comparison with the engineered surfaces. The mass transfer rate coefficients for these experiments are identified as $k_{pp}$.
3. Results & Discussion

3.1 Characterization of *H. pacifica* g cells

Analysis of the hydrophobicity (MATH test) data indicates 14.27±1.61% and 13.38±3.13% of *H. pacifica* g cells partition into the organic phase at 10mM and 100mM KCl, respectively. This suggests that these bacterial cells are predominantly hydrophilic at stationary growth phase as previously observed [34]. The bacterial cell zeta potentials were -58.7±2.61 mV and -19.94±6.53 mV at 10mM and 100mM KCl, respectively. This is also similar to what has been reported [18]. The zeta potential results indicate *H. pacifica* g cells were negatively charged over the range of ionic strength conditions tested, with the magnitude of the zeta potential decreasing with greater ionic strength.

3.2 Engineered Surface Characterization

Engineered surfaces were characterized for surface roughness, hydraulic diffusivity, static contact angle, and roll-off angle, and zeta-potential as shown in Table 2. Micro and nano-porous structures produced using the BDA, EPD, combined BDA with EPD, and spin coating of PDMS on either BDA or EPD modified substrates are visible in SEM images (Figure 2).

In the case of surfaces generated with the BDA technique (samples TiO$_2$-B-10°C and TiO$_2$-B-25°C), the irregular micro-scale features which resulted in surface roughness ~20 µm (Figure 2a, Table 2) are attributed to the competing mechanisms of dissolution and oxidation of the Ti plate during the anodization process without statistical significance due to heterogeneity (p > 0.05). Interestingly, the micro-porous structures
produced by the use of BDA have sub-micron thin channels on the surfaces, which are observed in SEM images (Figure 2a).

At low electrolyte temperatures the oxidation reaction was observed to dominate resulting in an increased substrate mass where at higher electrolyte temperatures (> 50 °C) rapid dissolution was observed which facilitated micro-pore formation. All TiO₂ BDA surfaces showed nearly zero contact angles because of the titanium oxide, which is the surface material after BDA, and a very hydrophilic material with rough surface structures, but hydraulic diffusivity was found to have statistical difference between TiO₂-B-10°C and TiO₂-B-25°C from 86 ± 10.56 mm²/s to 145 ± 3.42 mm²/s (p < 0.05). Hydraulic diffusivity is an indicator of the speed at which the liquid can move along a surface. Because TiO₂-B-25°C has higher surface roughness, which is known as proportional to the effective pore radius, less viscous drag can be expected than TiO₂-B-10°C, resulting in faster water propagation.

In contrast to BDA, EPD-generated surfaces are observed to be more uniform due to the deposition of uniformly size nanoparticles with nanopores between the coagulated particles (Figures 2b and 2d). Roughness occurs on the nanoscale for EPD generated surfaces (rather than on the microscale). For example EPD roughness (sample (P)SiO₂-E) is 1±0.09 µm significantly lower than the roughness produced using the BDA technique resulting in ~20 ± 10.17 µm roughness (samples TiO₂-b-10°C and TiO₂-B-25°C ) [32].
Figure 2. SEM images of the surfaces produced by the fabrication methods: breakdown anodization (BDA), electrophoretic deposition (EPD), and a spin coating with PDMS. The BDA surface consists of highly irregular entangled micro structures (a) while the surface deposited with TiO2 nanoparticles by EPD shows uniformly distributed nano-porous structures (b). Micro- and nano- porous structures are observed on the surface produced by the hybrid method of BDA and EPD (c). Deposits of hydrophobic SiO2 nanoparticles have nanoscale pores between agglomerated particles (d). The BDA surface coated with hydrophobic SiO2 nanoparticles show micro- and nano-porous structures (e). The BDA surface coated with PDMS by the spin-coating shows micro-bumps and PDMS coating layers between the structures (f). Surfaces (a)-(c) are superhydrophilic, surfaces (d)-(e) superhydrophobic, and surface (f) hydrophobic.
<table>
<thead>
<tr>
<th>Name</th>
<th>Fabrication method</th>
<th>Surface roughness (mm)</th>
<th>Hydraulic diffusivity ( (\text{mm}^2/\text{s}) )</th>
<th>Contact angle: ( q )</th>
<th>Roll-off angle: ( q )</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>N/A</td>
<td>((1.04\pm0.18)\times10^{-3})</td>
<td>0</td>
<td>24±4.1</td>
<td>41±2.94</td>
<td>-20</td>
</tr>
<tr>
<td>TiO(_2)-B-10°C</td>
<td>BDA</td>
<td>18±8.62</td>
<td>86±10.56</td>
<td>0</td>
<td>N/A</td>
<td>-0.1±5.83</td>
</tr>
<tr>
<td>TiO(_2)-B-25°C</td>
<td>BDA</td>
<td>23±12.37</td>
<td>145±3.42</td>
<td>0</td>
<td>N/A</td>
<td>11.8±8.74</td>
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<tr>
<td>TiO(_2)-BE</td>
<td>BDA + EPD</td>
<td>15±3.69</td>
<td>60±3.68</td>
<td>0</td>
<td>N/A</td>
<td>34.5±3.62</td>
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<tr>
<td>SiO(_2)-E</td>
<td>EPD</td>
<td>1±0.09</td>
<td>N/A</td>
<td>159±2.64</td>
<td>2±0.80</td>
<td>9.0±3.34</td>
</tr>
<tr>
<td>SiO(_2)-BE-25°C</td>
<td>BDA + EPD</td>
<td>21±10.12</td>
<td>N/A</td>
<td>147±3.45</td>
<td>14±3.08</td>
<td>19.2±3.32</td>
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<tr>
<td>SiO(_2)-BE-75°C</td>
<td>BDA + EPD</td>
<td>9±1.33</td>
<td>N/A</td>
<td>141±4.39</td>
<td>5±1.69</td>
<td>10.4±5.91</td>
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<tr>
<td>PDMS-B</td>
<td>BDA + PDMS</td>
<td>11±4.45</td>
<td>N/A</td>
<td>110±4.34</td>
<td>5±2.33</td>
<td>4.85±1.69</td>
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<tr>
<td>PDMS-E</td>
<td>EPD + PDMS</td>
<td>3±1.90</td>
<td>N/A</td>
<td>107±3.07</td>
<td>&gt; 90±4.78</td>
<td>-5.05±7.85</td>
</tr>
</tbody>
</table>

Table 2. The surface structures were characterized by a profilometer, and wetting properties were measured in terms of static contact angle, roll-off angle, and hydraulic diffusivity. Zeta potential was also measured at 10mM IS. Based on the contact angles, the prepared surfaces were classified as superhydrophobic (Samples TiO\(_2\)-B-10°C, TiO\(_2\)-B-25°C, TiO\(_2\)-BE), superhydrophilic (Samples SiO\(_2\)-E, SiO\(_2\)-BE-25°C, SiO\(_2\)-BE-75°C), and hydrophobic (Samples PDMS-B, PDMS-E).
When the method of BDA is followed by EPD for producing samples (TiO\textsubscript{2}-BE, (P)SiO\textsubscript{2}-BE-25\textdegree C and (P)SiO\textsubscript{2}-BE-75\textdegree C), dual scales of micro- and nano-porous structures were successfully produced on the surfaces (Figures 2c and 2e) as illustrated in Figure 1 on how these methods produce such structures. Since the layer deposited by EPD are uniform and thin (see Figure 2c and 2e), the microporous structures were maintained after being coated with nanoparticles. By coating BDA substrates with TiO\textsubscript{2} nanoparticles via EPD (sample TiO\textsubscript{2}-BE), the average surface roughness is slightly reduced by 3±10.82 µm in comparison to samples TiO\textsubscript{2}-B-10\textdegree C and TiO\textsubscript{2}-B-25\textdegree C; however, this was found to be insignificant due to heterogeneity of the surfaces (p > 0.05). BDA followed by EPD fabrication results in surfaces with wide ranges of surface roughness, hydrophobicity, and hydrophilicity (as shown in Table 2) dictated by the coating material (TiO\textsubscript{2}, (P)SiO\textsubscript{2}, or PDMS).

When BDA surface is coated with PDMS, microscale bumps are generated, resulting in PDMS being infused between the micro-structures (Figure 2f). Coating the BDA substrate with PDMS (sample PDMS-B) reduced roughness in comparison to sample TiO\textsubscript{2}-B-10\textdegree C, which was found to be insignificant due to physical heterogeneity of the samples. However, coating PDMS on the EPD surface slightly increases the surface roughness from 1 µm to 3 µm (p < 0.05). Interestingly, PDMS-B, and PDMS-E show similar static contact angles despite (SCA) having significantly different surface roughness. However, static contact angle measurements of surfaces coated with PDMS (samples PDMS-B, and PDMS-E) revealed contact angles greater 100\textdegree, reveling hydrophobic regions regardless of the underlying surface; and the hydrophobic surface
with micro-porous structures (PDMS-B) show a much lower roll-off angle than the nanoporous hydrophobic surface (PDMS-E). It was reported that hydrophobic surfaces (high static angles) with nano-scale rough structures may exhibit high roll-off angles (high stick force/high adhesion) associated with air trapped within pores [52, 53]. High adhesion results in a greater affinity of bacterial cells to surface and thus sample PDMS-B showing a lower contact angle and low roll off angle indicates for lower affinity.

The engineered surfaces were classified by their hydrophobicities, which are governed by the surface coating (i.e., TiO$_2$, (P)SiO$_2$ or PDMS). It was observed that the hydrophobicity was independent of preparation method (BDA, EPD, or spin coating). This was confirmed with TiO$_2$ (samples TiO$_2$-B-10°C, TiO$_2$-B-25°C, TiO$_2$-BE) layered surfaces, (P)SiO$_2$ layered surfaces (samples (P)SiO$_2$-E, (P)SiO$_2$-BE-25°C, (P)SiO$_2$-BE-75°C), and PDMS coated samples (PDMS-B, and PDMS-E) ranging in hydrophobicity from superhydrophilic, superhydrophobic and hydrophobic surfaces, respectively. BDA modified surfaces with or without TiO$_2$ nanoparticle coatings via EPD were found to be superhydrophilic as observed by the static contact angles of zero seen in Table 2. Thus hydraulic diffusivity was measured to identify the degree of hydrophobicity of these samples. This method determined sample TiO$_2$-BE was less hydrophilic than TiO$_2$-B-10°C because the nanoparticles coated on the BDA surface make smaller pore sizes and induce higher shear force. Based on the contact angles, samples prepared via EPD of (P)SiO$_2$ nanoparticles (coated with PDMS) and surfaces coated with PDMS (via spin coating) are classified as hydrophobic surfaces. Surfaces coated with (P)SiO$_2$ via EPD, are superhydrophobic surfaces with static contact angles greater than 140° (samples
(P)SiO2-E, (P)SiO2-BE-25°C, (P)SiO2-BE-75°C. Since the BDA method produces microscale rough-structures on the surface, samples (P)SiO2-BE-25°C and (P)SiO2-BE-75°C, show lower static contact angles than (P)SiO2-E, which has uniform nano-porous structures. It is known that microscale rough-structures are ineffective for enhancing the contact angles [54]. However our results indicate that nano-porous structures creating microscale roughness due indeed affect contact angles.

Quartz surfaces were used for the control surfaces in this work. The surfaces have an average static contact angle of 24 ± 4° but does not show the hydraulic diffusivity because the surfaces are too smooth (the average surface roughness is 1.04 ± 0.18 nm) to generate sufficient capillary pressure. Quartz grains have been shown to have zeta potentials of ~20 mV at 10 mM and ~10 mV at 100 mM [55]. We use these reference zeta-potentials as those of the quartz surfaces when the zeta-potential effects are investigated.

3.3 Bacterial Deposition on Quartz and Engineered Surfaces

Previous studies in the literature have shown that minimal deposition occurs on quartz at lower ionic strength conditions [55-58]. These deposition experiments were designed with the objective of quartz samples to be a comparison point of minimal deposition. Cell deposition on quartz was tested at 10 and 100 mM KCl, resulting in mass transfer rate coefficients of 2.98×10^{-9} ± 3.88×10^{-10} m/s and 1.43×10^{-8} ± 3.94×10^{-9} m/s respectively. Testing quartz below these IS shows deposition to become negligible, in
both parallel plate flow system and column studies [18, 55]. Measured mass transfer rate coefficients of quartz and engineered surfaces are shown in Figure 3a and 3b.

Engineered surfaces modified to produced hydrophilic samples TiO$_2$-B-10°C, TiO$_2$-B-25°C, and TiO$_2$-BE, had mass transfer rate coefficients of $1.25 \times 10^{-8} \pm 8.47 \times 10^{-9}$ m/s, $1.48 \times 10^{-8} \pm 2.86 \times 10^{-9}$ m/s and $1.56 \times 10^{-8} \pm 4.52 \times 10^{-9}$ m/s at 10 mM KCl. Comparison to quartz at 10 mM showed that sample TiO$_2$-B-10°C was not statistically different ($p > 0.05$) but samples TiO$_2$-B-25°C, and TiO$_2$-BE with greater values were found to be statistically different to quartz $k_{pp}$ values ($p<0.05$). At 100 mM KCl, the mass transfer rates coefficients where $1.60 \times 10^{-8} \pm 3.12 \times 10^{-10}$ m/s, $2.26 \times 10^{-8} \pm 5.68 \times 10^{-9}$ m/s and $2.06 \times 10^{-8} \pm 1.43 \times 10^{-9}$ m/s for samples TiO$_2$-B-10°C, TiO$_2$-B-25°C, and TiO$_2$-BE samples. At this IS, samples TiO$_2$-B-10°C and TiO$_2$-B-25°C were not statistically different from quartz $k_{pp}$ values ($p > 0.05$), but TiO$_2$-BE did show a statistical difference with greater $k_{pp}$ values compared to $k_{pp}$ quartz ($p < 0.05$), indicating that these surfaces will promote microbial attachment in comparison to the quartz samples.

The engineered surfaces prepared via deposition of PDMS coated SiO$_2$ ((P)SiO$_2$-E, (P)SiO$_2$-BE-25°C, and (P)SiO$_2$-BE-75°C) were found to be superhydrophobic and had $k_{pp}$ values of $6.94 \times 10^{-9} \pm 3.26 \times 10^{-9}$ m/s, $7.14 \times 10^{-9} \pm 6.16 \times 10^{-10}$ m/s and $5.56 \times 10^{-8} \pm 3.75 \times 10^{-9}$ m/s at 10 mM KCl, respectively. Samples (P)SiO$_2$-E and (P)SiO$_2$-BE-25°C were found to be statistically different to quartz, having larger $k_{pp}$ values ($p < 0.05$). (P)SiO$_2$-BE-75°C was found to have statistically insignificant deposition as with quartz ($p > 0.5$) at 10 mM KCl.
Figure 3. Mass transfer rates, $k_{pp}$, of *H. pacifica* onto quartz and novel surfaces in the parallel plate flow chamber systems at the ionic strength of (a) 10 mM KCl and (b) 100 mM KCl. Experiments carried out at temperature (22-25 °C) and ambient pH (5.6-5.8). Error bars indicate standard deviation.
Similar to what was observed for the TiO$_2$-based samples, there was an increase in mass transfer rate coefficients at the elevated ionic strength of 100 mM KCl (to 3.11×10$^{-8}$ ± 3.29×10$^{-9}$ m/s, 1.76×10$^{-8}$ ± 4.24×10$^{-9}$ m/s and 1.91×10$^{-8}$ ± 7.76×10$^{-9}$ m/s for (P)SiO$_2$-E, (P)SiO$_2$-BE-25°C, and (P)SiO$_2$-BE-75°C, respectively). At 100 mM KCl, (P)SiO$_2$-E sample was found to be statistically different than quartz due to great $k_{pp}$ values ($p < 0.05$) but (P)SiO$_2$-BE-25°C, and (P)SiO$_2$-BE-75°C were not found to statistically different ($p > 0.05$). Thus there was no clear trend distinguishing the superhydrophobic coatings and clean quartz.

The PDMS coated surfaces (PDMS-B and PDMS-E), resulted in surfaces that were hydrophobic and showed mass transfer rates coefficients of 1.68×10$^{-9}$ ± 8.71×10$^{-10}$ m/s and 2.80×10$^{-9}$ ± 3.92×10$^{-10}$ m/s at 10 mM KCl, respectively. The $k_{pp}$ value of PDMS-B is significantly less than quartz at 10 mM ($p > 0.05$). Values at 100 mM which were found to be 9.55×10$^{-9}$ ± 1.68×10$^{-9}$ m/s and 1.56×10$^{-9}$ ± 1.82×10$^{-9}$ m/s. In comparison to quartz at 100 mM, PDMS-B showed the less cell attachment rate with a statistical difference of $p > 0.05$. The treatment with PDMS on micro-porous surfaces produced by BDA resulted in deposition less than that of quartz, effectively indicating that BDA and EPD surface overlaid with poly(dimethyl siloxane) (PDMS) appeared to be most resistant to cell attachment.

3.4 Mechanisms of Attachment

Greater deposition rates were observed under higher ionic strength. The intensity of electrostatic repulsion between Figure 3a and 3b shows sensitivity to the IS of the
solution [59]. Increased IS resulted in a decrease in electrostatic repulsive forces, leading to increased bacterial cell attachment as noted in Figures 3a and 3b. All samples showed sensitivity for IS therefore electrostatic interactions significantly governed cell deposition.

Test surfaces TiO$_2$-B-10°C, TiO$_2$-B-25°C, TiO$_2$-BE had the greatest deposition of cells as anticipated due to their superhydrophilic nature, which interacted favorably with the highly hydrophilic cells of $H. pacifica$ g. Engineered superhydrophobic surfaces (P)SiO$_2$-E, (P)SiO$_2$-BE-25°C, and (P)SiO$_2$-BE-75°C were expected to have the least amount of bacterial cells deposit; however, they showed greater deposition than that of the hydrophobic surfaces (PDMS-B and PDMS-E). Test surfaces PDMS-B, and PDMS-E showed deposition of cells to be similar to or less than quartz samples; There is potential for future applications of PDMS as the primary strategy to achieve an antifouling surface, which has been corroborated by other studies[60]

Mass transfer rates of cells onto the hydrophilic surfaces (TiO$_2$-B-10°C, TiO$_2$-B-25°C, and TiO$_2$-BE) and quartz  as are shown in Figure 4a as function of roughness. There is a correlation with increased roughness as $k_{pp}$ values are increased. In Figure 4b there is further indication that hydrophilicity was dependent on roughness; therefore these samples are sensitive to roughness only. This is supported by a previous study reporting roughness attributes to overall attachment, and thus promoting bacterial adhesion [61].

The mass transfer rate coefficients of the $H. pacifica$ g on hydrophobic samples (P)SiO$_2$-E, (P)SiO$_2$-BE-25°C, (P)SiO$_2$-BE-75°C, PDMS-B, and PDMS-E in comparison to roughness are shown in Figure 5a.
Figure 4. Mass transfer rates, $k_{pp}$ of $H.\ pacifica$ compared to (a) roughness at both 10 mM KCl and 100 mM KCl and indicating a slight increase in $k_{pp}$ values with increase in roughness (b) hydraulic diffusivity and indicates hydrophilicity is not a factor in $k_{pp}$ value.
Figure 5. Roughness of surfaces covered in PDMS in comparison to (a) mass transfer rates, $k_{pp}$, of *H. pacifica* g at 10 mM KCl and 100 mM KCl showing a slight decrease with increase of roughness but not definitive (b) contact angle values indicating a slight effect of roughness for a majority of sample.
There may be a correlation with roughness and $k_{pp}$ values; however, we were unable to quantify this due to the limited sampling. The trend suggests (Figure 5a) that the $k_{pp}$ values slightly decrease with increase roughness but it is uncertain if the trend plateaus plentifully or may continue to increase. Therefore, there is opportunity to optimize roughness such that we can reduce microbial adhesion. There is a more apparent impact at the higher IS condition (100 mM) as seen in Figure 5a, which is comparable to more brackish waters indicating that surface roughness may be exploited in such systems for controlling cell attachment. There is also a correlation between contact angle and roughness in hydrophobic surfaces as shown in Figure 5b, which indicates a slight increase in contact angle as roughness is increased for comparable samples.

3.5 Conclusion

We have investigated cell attachment via the mass transfer coefficients on different engineered surfaces produced by EPD, BDA, and spin coating with PDMS. The resulting surfaces showed hydrophobicity ranges from superhydrophilic to superhydrophobic with different rough scales and nano-porous and micro-porous structures produced by EPD of nanoparticles and BDA with PDMS spin coating, respectively. The effects of the different roughness scales were reflected especially by the roll-off angles on hydrophobic surfaces, showing low roll-off angles on micro-scale rough surfaces.

“Anti-fouling” surfaces, as defined as surfaces with mass transfer rates similar to quartz surfaces, were successfully produced by BDA and spin coating with PDMS
(sample PDMS-B). From the SEM images and the surface roughness data, the surfaces are composed of micron scale bumps and relatively large surface roughness. The surface characteristics were indicated by hydrophobic surfaces with 110° static contact angles and of 5° roll-off angles, attributed by PDMS and the micro-scale rough structures.

The engineered surfaces, which were superhydrophilic, displayed higher mass transfer rates than the hydrophobic and superhydrophobic surfaces. This observation was due to the favorable interaction found between the hydrophilic bacterial cells with superhydrophilic surfaces. The difference of mass transfer rates between the hydrophobic surfaces decreased with greater ionic strength because the electrostatic interactions overwhelmed other interaction forces.

The incorporation PDMS coated SiO$_2$ and TiO$_2$ nanoparticles increased mass transfer to the surface as compared to pure BD techniques for each engineered surface. For example, TiO$_2$-BE, SiO$_2$-E, and PDMS-E showed greater mass transfer rates than TiO$_2$B-10°C and -25°C, SiO$_2$-BE-25°C and -75°C, and PDMS-B, respectively. Thus indicating that the presence of nanoscale structures created sufficient roughness as to enhance cell-attachment.

The engineered hydrophobic surface PDMS-B showed lower mass transfer rates than PDMS-E even though static contact angle data showed no difference between two surfaces. This was due to PDMS-B having more micro structures, which can be verified from roll-off angles and also roughness data. PDMS-B revealed much lower roll-off angles than PDMS-E indicating that PDMS-B has less nano scale rough structures than
PDMS-E. It is well known that nano structures enhance contact angle hysteresis, resulting in high roll-off angle [52].

Results indicate that TiO$_2$-BE presented the greatest mass transfer rates because it is superhydrophilic and has nano structures attributed to the TiO$_2$ nanoparticles deposited by EPD on the micro-porous structures produced by BDA. However, PDMS-B showed the best “anti-fouling” performance due to its hydrophobicity and micro-porous structures. Therefore, in the case of hydrophilic bacteria, we can expect that surfaces that are hydrophobic and have low roll-off angles will be the best candidates for anti-fouling performance. In contrast, superhydrophilic surfaces that have nano rough structures will likely induce biofouling.

These novel engineered surfaces show properties that can be functional to a variety of industries. Engineered surfaces produced by breakdown anodization that were spin coated with PDMS (sample PDMS-B) have the potential for applications on various marine surfaces (i.e. ship hulls). These surfaces showed similar results to our control samples (quartz) and may be the most durable of the engineered surfaces. The ionic strengths tested indicate that these PDMS coated surfaces would be best for fresh water or brackish systems. This work has demonstrated that through these engineering approaches, we have the ability to alter surfaces at the nano- and micro- scale by a combination of techniques. This gives potential for manipulation and thus allowing for fine-tuning the properties of the materials for the particular aquatic environment in question.
References


