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# Modification of Silicone Elastomer Surfaces with Zwitterionic Polymers: Short-Term Fouling Resistance and Triggered Biofouling Release

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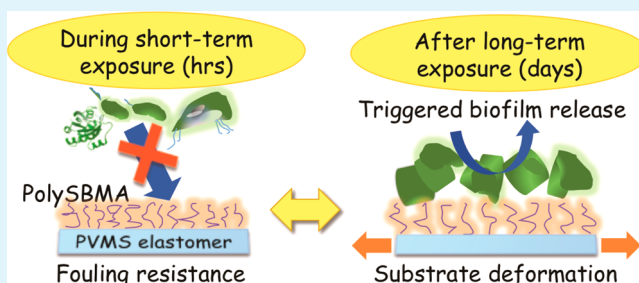
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## S Supporting Information

**ABSTRACT:** We present a method for dual-mode-management of biofouling by modifying surface of silicone elastomers with zwitterionic polymeric grafts. Poly(sulfobetaine methacrylate) was grafted from poly(vinylmethylsiloxane) elastomer substrates using thiol–ene click chemistry and surface-initiated, controlled radical polymerization. These surfaces exhibited both fouling resistance and triggered fouling-release functionality. The zwitterionic polymers exhibited fouling resistance over short-term (~hours) exposure to bacteria and barnacle cyprids. The biofilms that eventually accumulated over prolonged-exposure (~days) were easily detached by applying mechanical strain to the elastomer substrate. Such dual-functional surfaces may be useful in developing environmentally and biologically friendly coatings for biofouling management on marine, industrial, and biomedical equipment because they can obviate the use of toxic compounds.

**KEYWORDS:** silicones, elastomers, zwitterionic polymers, fouling-resistance, biofouling



Biofouling, i.e., the accumulation of biomolecules, cells, and organisms on wetted surfaces, is a ubiquitous problem in maritime operations, medicine, food industries, and biotechnology.<sup>1,2</sup> Many of the current commercial coatings for marine equipment (e.g., ship hulls) rely on antifouling paints that leach out broad-spectrum biocides (e.g., copper oxide, copper thiocyanate) to resist the surface accumulation of fouling species.<sup>3</sup> Because of the deleterious effects of such biocides in aquatic environments, there is a pressing need for alternative, effective and eco-friendly coatings.<sup>3,4</sup> Silicone-based surfaces have been of great interest in marine, biotechnological and medical contexts, mainly because they are nontoxic and exhibit low surface adhesion strength to biofoulants, which can be easily removed using surface cleaning methods (e.g., water jets, grooming). Although the exact mechanism of silicone fouling-release behavior is still incompletely understood, it has been attributed to a combination of surface properties, including low surface energy,<sup>4,5</sup> low modulus,<sup>6</sup> and surface-enrichment of silicone oils (oligomers), which can have a number of effects, both physical<sup>7</sup> and biological (e.g., inhibition of enzymatic activity<sup>8</sup>).

Biomimetic surface topologies,<sup>9</sup> polymer brushes,<sup>10–13</sup> amphiphilic block copolymers,<sup>4</sup> and oil infused surfaces<sup>7,14</sup> can be effective against short-term biofouling (and are referred to herein as fouling-resistant surfaces). While promising, there is growing consensus that all of the fouling-resistant surfaces developed thus far eventually succumb to surface-colonizing species in complex marine and biomedical aqueous milieus.<sup>1,14–16</sup> Hence, there is need to develop bifunctional coatings that can synergistically exhibit both fouling-resistance and fouling-release properties, and thus enable multipronged, proactive approaches to biofouling management.<sup>4,10</sup> We recently showed that dynamic change of surface area of elastomers (i.e., cyclic deformation beyond a critical strain) effectively detaches biofilms and barnacles.<sup>17–19</sup> Electro-, pneumatic-, and direct mechanical-actuation were used as external stimuli to generate controlled and on-demand surface deformation of silicone elastomers.

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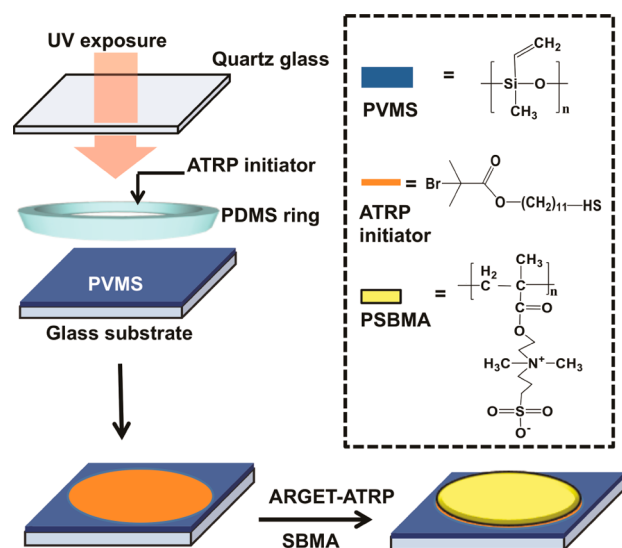
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The objective of this study was to develop a method to tailor the surface properties of silicone elastomers using polymers that have fouling-resistant properties. We hypothesized that biofouling-resistant polymers grafted from such elastomers can be used as a bifunctional surfaces, which (i) prevent short-term fouling and (ii) can undergo mechanical strain to detach biofilms that accumulate over prolonged exposure to a fouling environment.

Poly(dimethylsiloxane) (PDMS)-based elastomers are often used as model silicone fouling-release surfaces for biofouling studies. Previous reports on surface modification of PDMS with fouling-resistant polymers have involved physical methods for surface oxidation (e.g., oxygen plasma or ultraviolet/ozone treatment) as an intermediate step prior to reaction with silane coupling agents.<sup>20,21</sup> Use of such methods can dramatically increase the surface modulus by forming a stiff silica-like layer,<sup>22</sup> which may reduce fouling-release properties.<sup>4,6</sup> It was previously reported that brief ultraviolet (UV) irradiation of poly(vinylmethylsiloxane) (PVMS)-based elastomers in the presence of alkylthiol molecules does not significantly alter the modulus, and can be used to produce high-surface-density self-assembled monolayers (SAMs) via thiol–ene click chemistry.<sup>23</sup> We used this approach to graft initiators on PVMS, which were used to grow zwitterionic polymers from silicone surfaces using activators regenerated by electron transfer for atom transfer radical polymerization (ARGET-ATRP).<sup>12,24</sup>

The method we used to modify PVMS surfaces is illustrated in Scheme 1. The elastomer surfaces were prepared using a

Scheme 1.<sup>a</sup>



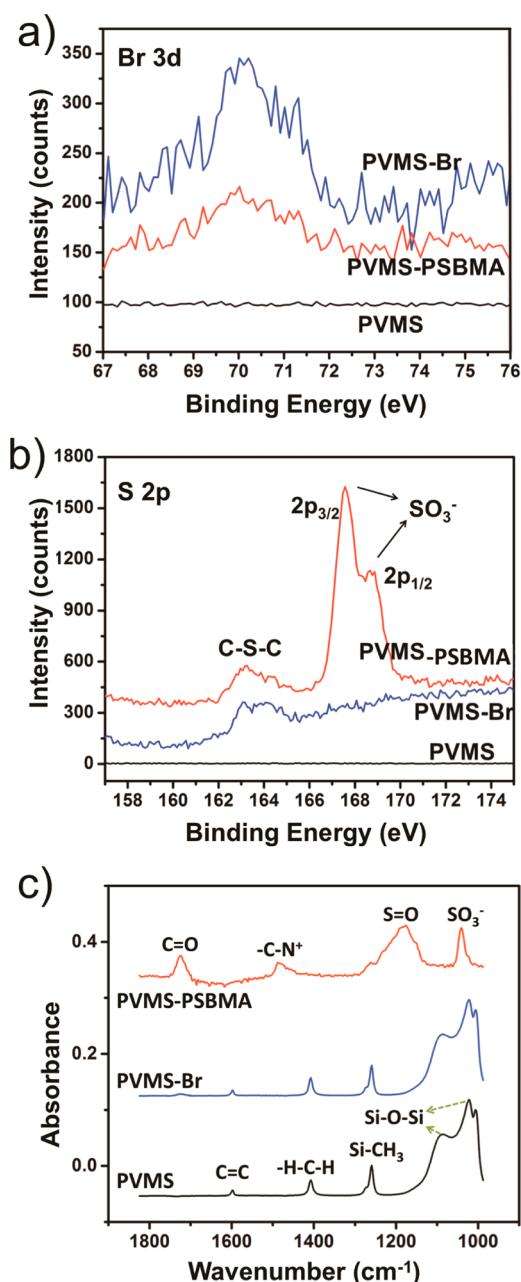
<sup>a</sup>A PVMS elastomer coating (thickness  $\sim 500\ \mu\text{m}$ ) cured on a glass substrate was covered with 2 mM ATRP initiator contained in a PDMS ring. The top surface was then briefly exposed to UV light ( $\lambda = 254\ \text{nm}$ ) to immobilize ATRP-initiator and followed by ARGET-ATRP to graft PSBMA.

previously established method: a precursor mixture was spin-coated on clean glass slides ( $25\ \text{mm} \times 25\ \text{mm}$ ) and cured at  $65\ ^\circ\text{C}$  for 2 h. The PVMS precursor mixture comprised an oligomer, a cross-linker, a catalyst, and filler particles (see the Supporting Information). We fabricated a ring of silicone rubber (Sylgard 184, Dow Corning) and placed it on the cured PVMS to contain an ethanolic solution of 2 mM of  $\omega$ -mercaptoundecyl bromoisobutyrate (the ATRP-initiator). This

solution on the PVMS was exposed to UV light ( $\lambda = 254\ \text{nm}$ ,  $8\ \text{W}/\text{cm}^2$ , Spectrolinker XL-1500, Spectroline Inc. USA) for 5 min through a thin quartz glass. Under UV exposure, the thiol-terminated initiator molecules reacted with the vinyl groups on the surface of PVMS via a thiol–ene reaction (the reaction product is denoted herein as PVMS-Br). After thorough rinsing of the PVMS-Br surface, a surface-initiated ARGET-ATRP reaction developed by Matyjaszewski et al.<sup>24</sup> was conducted for 30 min to grow poly(sulfobetaine methacrylate) (PSBMA). The detailed ARGET-ATRP reaction procedure and schematic are provided in Figure S1. ARGET-ATRP was used because it offers a simple method to graft uniform polymers without requiring the necessity for oxygen-free reaction conditions. In this application, given that silicone elastomers are porous and readily absorb air, the ARGET-ATRP approach may be especially advantageous over conventional ATRP. Zwitterionic PSBMA was considered in this study because it has been shown to offer fouling-resistance toward a variety of biofouling agents.<sup>11</sup>

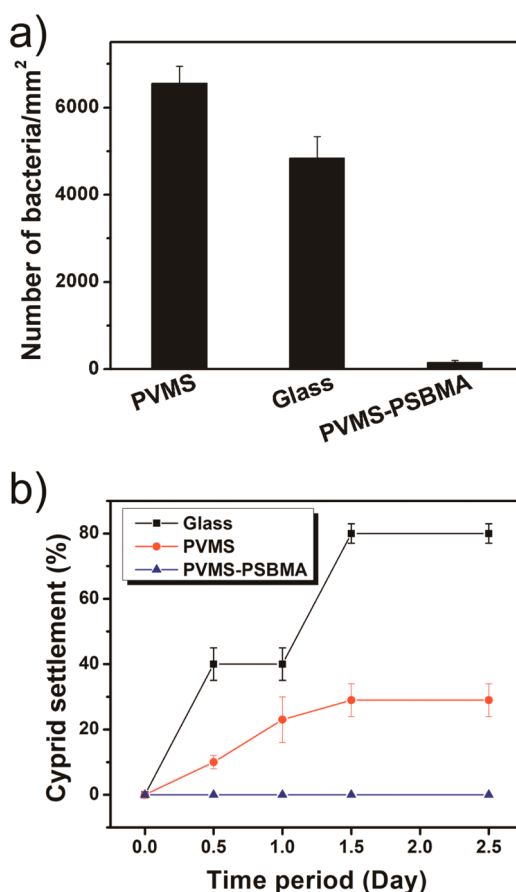
The PVMS-Br and PSBMA-modified PVMS (denoted herein as PVMS-PSBMA) surfaces were characterized using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and static water contact angle (CA) measurements. On PVMS-Br, the bromine XPS peak (Figure 1a) at 69.8 eV suggests the presence of ATRP-initiator and the sulfur peak (Figure 1b) at  $\sim 164\ \text{eV}$  represents the bonds formed between sulfhydryl groups of ATRP-initiator and vinyl groups on PVMS (C–S–C). This confirms the successful covalent attachment of the initiator to the PVMS surface. For PVMS-PSBMA samples, the XPS sulfur peak ( $\text{SO}_3^-$  peak at  $\sim 168\ \text{eV}$ ) and carbon peaks (C–N/C–S and O–C=O at 286.6 and 287.4 eV, respectively) (Figure 1b and Figure S2) confirm the presence of PSBMA. FTIR spectra (Figure 1c) show absorption peaks corresponding to C=C ( $1590\ \text{cm}^{-1}$ ) on both PVMS and PVMS-Br, which suggest that the thiol–ene coupling is restricted to the surface of PVMS and does not occur appreciably within the bulk of the elastomer. The absorption spectrum of PVMS-PSBMA (Figure 1c) shows distinct peaks when compared against PVMS and PVMS-Br. The absorption peaks corresponding to C=O ( $1725\ \text{cm}^{-1}$ ), C–N ( $1490\ \text{cm}^{-1}$ ), and asymmetric stretching of S=O ( $1180\ \text{cm}^{-1}$ ) are characteristic of PSBMA and confirm successful grafting of the zwitterionic polymer from the PVMS-Br surface. The CAs measured show (Figure S2b) a significant difference between PVMS ( $105 \pm 3^\circ$ ) and PVMS-PSBMA ( $32 \pm 2^\circ$ ). The relatively low CA on PVMS-PSBMA reflects the high degree of solvation due to strong interactions of PSBMA with water. To summarize, the results from XPS, FTIR and CA measurements confirm that the surface of PVMS was modified with PSBMA polymer using thiol–ene coupling and ARGET-ATRP. It was not feasible to measure the thickness of the grafted PSBMA using ellipsometry directly because the PVMS elastomer is optically clear, so we grafted PSBMA from ATRP-initiator immobilized on gold surfaces under similar reaction conditions and measured the dry thickness of PSBMA on gold surfaces (Au-PSBMA) using ellipsometry. The measured thickness of polymer on Au-PSBMA was  $28 \pm 3\ \text{nm}$ , which is our best estimate of the dry thickness of PSMA on PVMS-PSBMA.

To test the hypothesis that zwitterionic polymer-modified silicones exhibit fouling-resistance, multiple replicates of PVMS-PSBMA, PVMS and clean glass substrates were subjected to suspensions of a model, Gram-negative, marine



**Figure 1.** XPS high-resolution spectra (a) Br-3d and (b) S-2p and (c) FTIR absorption spectra of PVMS, PVMS-Br, and PVMS-PSBMA.

bacterium, *Cobetia marina* ( $1 \times 10^7$  cells/mL in 0.85% NaCl) for 2 h at 22 °C. The surfaces were then very gently rinsed with ultrapure water, dried in air, imaged using phase contrast microscopy and analyzed to determine surface density of cells. Figure 2a summarizes the results of surface density of attached cells. Glass and PVMS surfaces exhibited high densities of cell attachment ( $>4,500$  cells/mm<sup>2</sup>), whereas PVMS-PSBMA exhibited low cell density ( $<200$  cells/mm<sup>2</sup>). This corresponds to  $>95\%$  reduction of cell attachment on PVMS-PSBMA. Zwitterionic polymers, because of their strong electrostatically induced hydration, form a tightly bound water layer in the vicinity of polymer chains, which can prevent the attachment of microbes and other fouling species.<sup>10,11,25</sup> The cell morphology of the attached *C. marina*, imaged using scanning electron microscopy, was similar on both PVMS (control) and PVMS-PSBMA (Figure S3a), suggesting that PSBMA does not



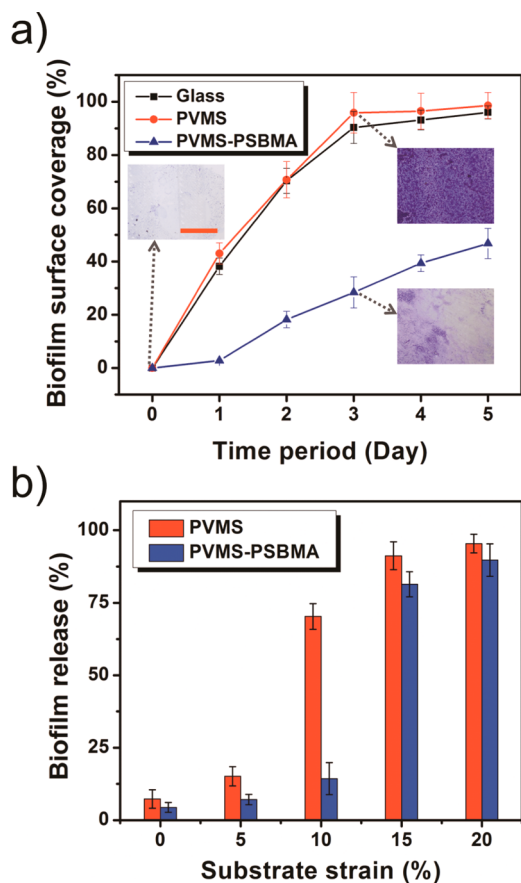
**Figure 2.** (a) Attachment density of *C. marina* on glass, PVMS and PVMS-PSBMA after exposure to  $1 \times 10^7$  cells/mL for 2 h at 22 °C. (b) Percentage of barnacle cyprids settled over a period of 2.5 days on glass, PVMS and PVMS-PSBMA. The error bars in a and b correspond to the standard deviation of the mean ( $n = 5$ ).

influence cell structure. PVMS-PSBMA also showed resistance to nonspecific protein adsorption in comparison to PVMS (Figure S3b) as well. These results suggest that PVMS-PSBMA exhibits short-term fouling resistance.

Figure 2b presents the results of settlement of barnacle cyprids, *Amphibalanus* (= *Balanus*) *amphitrite*,<sup>26</sup> on glass, PVMS and PVMS-PSBMA test surfaces. Barnacles are common nonmotile macro-fouling species that attach to surfaces in the last larval, cyprid, stage after which they metamorphose into juvenile barnacles. Large drops of seawater containing 5–10 cyprids were carefully placed on each test substrate and allowed to settle for a period of 2.5 days (see the Supporting Information for detailed procedure). PVMS-PSBMA test surfaces inhibited the settlement of cyprids for the entire duration of the study, whereas glass and PVMS experienced increasing amounts of cyprid settlement with time (Figure 2b). On PVMS-PSBMA, it was observed cyprids became trapped in the aqueous seawater layer and later died after 24 h (Figure S3c). It has been reported that entrapping of cyprids delays their metamorphosis, which, in turn, often influences their growth and survival.<sup>27</sup> These results are in agreement with previous assays of settlement on zwitterionic polymer brushes grafted from glass and Au-coated substrates.<sup>11,28</sup> In summary, the results in Figure 2 support the hypothesis that PVMS modified with zwitterionic polymers can inhibit biofouling over short-time intervals.



To examine the fouling of PVMS–PSBMA over longer-terms, multiple replicates of PVMS–PSBMA, PVMS and glass surfaces were exposed to suspensions of *C. marina* for 1–5 days (see SI for procedure), after which each test surface was gently rinsed with sterilized artificial seawater (ASW), stained with 0.1% crystal violet (aqueous), dried in air and photographed. The surface biofilm coverage was estimated by converting the color images to binary scale using ImageJ software and adjusting the threshold to precisely differentiate between areas with, and without, visible biofilm.<sup>18</sup> The rate of biofilm formation on PVMS–PSBMA was slower than on glass or PVMS. PVMS and glass surfaces had >80% biofilm surface coverage within 3 days, whereas PVMS–PSBMA had ~45% biofilm coverage in 5 days (Figure 3a). When the fouling time



**Figure 3.** (a) Surface coverage of *C. marina* biofilms on glass, PVMS, and PVMS–PSBMA surfaces over a time period of 5 days. The insets are photographs of crystal violet stained biofilms on PVMS and PVMS–PSBMA after 0 and 3 days; the scale bar corresponds to 2.5 mm. (b) The percentage of *C. marina* biofilm (grown for 14 days) released from PVMS and PVMS–PSBMA surfaces under a range (0–20%) of applied strain. The error bars in a and b correspond to the standard deviation of the mean ( $n = 5$ ).

period was extended to 2 weeks, > 97% of PVMS–PSBMA surface was covered with biofilm (Figure S4a), indicating that fouling resistance of PVMS–PSBMA diminishes upon longer-term exposure to biofouling conditions. This could be due to various factors, for example, to instability of hydrated polymer chains in aqueous solution over longer time-intervals, or to a steady overcoming of the hydration layer resistance of the PVMS–PSBMA by *C. marina* to result in the accumulation of microbes on the surface over time.<sup>16,29</sup>

Lopez, Zhao, and co-workers recently reported that biofilms accumulated on silicone elastomers can be efficiently released by active deformation of the surface.<sup>17–19</sup> Surface deformation can be achieved by various means, for example, by directly stretching the elastomer or by using more indirect methods, such as electro- and pneumatic-actuation. In this study, we examined the hypothesis that biofilms accumulated on PSBMA-modified silicones can be released using surface deformation. PVMS elastomer coupons (25 mm × 10 mm) of 3 mm thickness were prepared by curing the precursor mixture in a 3D printed plastic mold. The cured elastomer was removed from the mold and PSBMA was grafted on one side of the film surface (see Scheme 1) using surface-initiated ARGET-ATRP. To examine the mechanical stability of the grafted polymer under substrate deformation, we subjected PVMS–PSBMA films to uniaxial strain of 50% for at least 20 cycles using a tensile tester (Test Resources, USA). The films were then sonicated in DI water, dried in nitrogen gas and analyzed by XPS. The elemental composition of PVMS–PSBMA surface before and after stretching was almost identical (Table S1) suggesting that the polymer layer on the PVMS was stable after repeated substrate deformation.

To examine whether surface deformation can detach biofilms accumulated on polymer-modified silicones, multiple replicates of PVMS–PSBMA and PVMS (control) films were subjected to *C. marina* biofilm formation for 14 days. Each test surface with biofilm was carefully subjected to 15 cycles of fixed (5, 10, 15, or 20%) uniaxial strain, at a constant strain rate (50 mm/min). The films were then gently rinsed (5 mL/min for ~2 min) with sterilized ASW and analyzed for surface biofilm coverage using the procedure detailed above. The percentage of biofilm released was estimated by taking the ratio of surface coverage of biofilm before and after the deformation.<sup>18</sup> Figure 3b illustrates the percentage of biofilm released from PVMS and PVMS–PSBMA surfaces after they were subjected to under various amounts of applied strain (Figure S4 shows representative images of the crystal-violet-stained biofilms on test surfaces before and after application of cyclic strain and rinsing). For low substrate strains ( $\epsilon$ ) of 0 or 5%, no significant biofilm release was observed, but at higher strains, substantial release of biofilm occurred (e.g., for  $\epsilon > 10\%$  for PVMS;  $\epsilon > 15\%$  of PVMS–PSBMA more than 85% of the biofilm was released). Zhao et al. postulated that elastic energy per unit area in the biofilm increases with substrate strain and when this energy exceeds the biofilm–substrate adhesion energy, the biofilm debonds from the substrate.<sup>17</sup> The debonded biofilm can then be easily removed upon gentle rinsing. Figure 3b and Figure S4 show that the value of  $\epsilon$  required for release of the *C. marina* biofilms was lower for PVMS ( $\approx 10\%$ ) than that for PVMS–PSBMA ( $\approx 15\%$ ). This observed difference could be due to a number of factors.<sup>18,19</sup> For instance, the biofilm thickness and/or the Young's modulus (both of which have been postulated to effect the critical strain necessary for biofilm debonding<sup>17,19</sup>) may also depend on the substrate upon which it forms. In this study, the slower rate of biofilm accumulation on PVMS–PSBMA observed (Figure 3a) suggests that the biofilm formed on PVMS–PSBMA may be thinner than on PVMS at the 14 day time point when they were subjected to strain treatment.

Finally, we examined whether the PVMS–PSBMA film after biofilm detachment could exhibit and retain fouling resistance when reimmersed in a fouling environment. PVMS–PSBMA exhibited fouling resistance (Figure S5), but to a lesser extent

(e.g.,  $37 \pm 2\%$  biofilm coverage in 3 days) as compared to a pristine PVMS–PSBMA surface (Figure 3a). This suggests that the fouling resistance of PVMS–PSBMA may reduce over repeated cycles of biofilm formation; such reduction may be alleviated by improvements in the performance and stability of zwitterionic polymers.<sup>29</sup>

This study presents a chemical approach to easily modify the surface properties of PVMS-based elastomers with fouling resistant zwitterionic polymers. This chemical modification approach is applicable to grafting other types of biofunctional polymers as well (e.g., thermoresponsive poly(*N*-isopropylacrylamide) which provides another mechanism for triggered-fouling release as detailed in Figure S6). Biofilms accumulated on zwitterionic PSBMA polymers over long-term fouling exposure are effectively released by applying mechanical strain to the PVMS substrate. These types of bifunctional surfaces may be applicable for pro-active biofouling management on marine equipment (e.g., ship hulls, sensors), industrial equipment<sup>2</sup> and biomedical devices (e.g., urinary catheters<sup>18</sup>) and can be implemented with electro- or pneumatic-actuation systems,<sup>17</sup> for example.

The design of long-term, fouling-resistant surfaces provides extraordinary challenges, because biofouling environments can consist of myriad, and often cooperatively interacting, surface-active species. To the best of our knowledge, so far, none of the fouling-resistant surface modification strategies developed resist biofouling in the long term. The substrate deformation approach presented in this study for zwitterionic fouling resistant surfaces should also be applicable to other existing and emerging<sup>30</sup> types of fouling-resistant strategies as well.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b09199.

Materials and methods, Figures S1–S6, and Table S1 (PDF)

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

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