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Antifouling silicones based on surface-modifying additive amphiphiles

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Abstract

Surface modifying additives (SMAs), which may be readily blended into silicones to improve anti-fouling behavior, must have excellent surface migration potential and must not leach into the aqueous environment. In this work, we evaluated the efficacy of a series of poly(ethylene oxide) (PEO)-based SMA amphiphiles which varied in terms of crosslinkability, siloxane tether length (m) and diblock versus triblock architectures. Specifically, crosslinkable, diblock PEO-silane amphiphiles with two oligodimethylsiloxane (ODMS) tether lengths [$(EtO)_3Si$-$(CH_2)_3$-$ODMS_m$-PEO_8, m = 13 and 30] were compared to analogous non-crosslinkable, diblock (H-Si-$ODMS_m$-PEO_8) and triblock (PEO_8-$ODMS_m$-PEO_8) SMAs. Prior to water conditioning, while all modified silicone coatings exhibited a high degree of water-driven surface restructuring, that prepared with the non-crosslinkable diblock SMA (m = 13) was the most hydrophilic. After conditioning, all modified silicone coatings were similarly hydrophilic and remained highly protein resistant, with the exception of PEO_8-$ODMS_{30}$-PEO_8. Notably, despite twice the PEO content, triblock SMAs were not superior to diblock SMAs. For diblock SMAs, it was shown that water uptake and leaching were also similar whether or not the SMA was crosslinkable.

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Keywords

ANTI-FOULING; POLYMERIC MATERIALS; SURFACE MODIFICATION

1. Introduction

While silicones favorably exhibit non-toxicity, biostability and elastomeric mechanical properties,[1, 2] their poor anti-fouling behavior limits their efficacy for blood-contacting medical devices as well as non-toxic marine coatings. It is the extreme hydrophobicity of silicones which gives rise to its adhesiveness to a variety of biofoulers, such as proteins[3–5] and marine organisms.[6, 7] When silicones contact blood, the rapid adsorption of plasma proteins (e.g. fibrinogen) induces platelet adhesion and activation which leads to thrombus formation.[4, 5, 8] For devices such as dialysis catheters, thrombosis can obstruct blood flow and facilitate infection.[9–11] Biofouling of ship hulls generally results from the adhesion and accumulation of proteins followed by bacteria, diatoms, and other microorganisms, resulting in increased hydrodynamic drag and subsequently greater fuel consumption and maintenance costs.[6, 12–14] Historically, marine biofouling has been attempted to be controlled through the use of toxic, ablative coatings which negatively impact non-target marine life and ecosystems. Towards reducing biofouling for these two applications, a non-toxic strategy to produce protein resistance is highly sought after, as this is typically indicative of broader anti-fouling behavior. While silicones are adhesive to proteins and other biofoulers, hydrophilization of silicone with physical, chemical, and combined strategies has been generally shown to improve anti-biofouling behavior.[5, 15–19]

Silicone modification with poly(ethylene oxide) (PEO) [or poly(ethylene glycol) (PEG)] has been studied towards increasing surface hydrophilicity and protein resistance.[20–25] This is motivated by the exceptional ability of PEO to resist protein adsorption which is attributed to the formation of a repulsive hydration layer, steric repulsion and blockage of surface adsorption sites.[26–29] The protein resistance of PEO has been largely demonstrated when applied to model substrates such as gold,[30–32] glass,[33, 34] and silicon wafer.[35–38] While considered biocompatible[39] and oxidatively stable in biological conditions,[40] the *in vivo* protein resistance of PEO-modified polymeric materials has been observed to be limited and inconsistent.[41–43] Thus, the method of incorporation of PEO into polymers such as silicones is critical to achieving surface hydrophilicity and protein resistance.

“Surface modifying additives” (SMAs), while incorporated into a base polymer in relatively small amounts via simple bulk modification (i.e. blending), are intended to migrate to the air or solution interface to affect surface modification.[44, 45] SMA strategies are an attractive option for surface modification as they avoid the complications associated with poor adhesion of the coatings to substrates and complex surface grafting methods. SMAs have been reported for several base polymers and are typically amphiphilic diblock or triblock oligomers where the hydrophobic block has an affinity to the base polymer.[44, 46] A PEO-based SMA for silicones must give rise to an adequately high PEO surface concentration,[32, 36, 47, 48] specifically at the aqueous (i.e. biological) interface where protein adsorption occurs. In the case of the aforementioned “model PEO surfaces”, PEO chains are retained at

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the surface whether in air or in an aqueous environment. Silicones, however, are able to undergo substantial surface reorganization depending on their exposure to an air or aqueous environment.[49] This process has been mostly studied in the case of hydrophobic recovery such as when plasma-treated silicone surfaces return to a hydrophobic state if maintained in air but remain hydrophilic if stored in water.[50] This behavior stems from the low surface energy[51] and high chain flexibility[52] of silicones. Hydrophobic recovery is also observed for silicones bulk modified with conventional PEO-silanes such as triethoxysilylpropyl PEO monomethyl ether [$(EtO)_3Si$-$(CH_2)_3$-PEO_n-OCH_3][20, 21] and allyl PEO monomethyl ether [CH_2=$CHCH_2$-PEO_n-OCH_3].[22] Following hydrophobic recovery, PEO may have a limited potential to migrate to the aqueous interface.

To induce surface hydrophilicity and protein resistance, a PEO-based SMA incorporated into silicones must undergo appreciable water-driven restructuring to the surface. We have shown that for RTV silicones bulk-modified with conventional PEO_n-silanes (n = 3, 8 and 16), poor water-driven surface restructuring of PEO was observed leading to high protein adsorption similar to that of unmodified silicone.[53] In contrast, PEO-silane amphiphiles comprised of an oligodimethylsiloxane (ODMS) tether and crosslinkable triethoxysilane (TEOS) group [α-$(EtO)_3Si$-$(CH_2)_3$-$ODMS_{13}$-*block*-PEO_8-OCH_3] dramatically increased water-driven surface hydrophilicity and reduced the adhesion of proteins[53–55] and other biofoulers.[56, 57] Extensive atomic force microscopy (AFM) analysis was used to verify the water-driven migration of PEO to the silicone surface.[58] For this class of PEO-silane amphiphiles, we have previously shown that siloxane tether length (m)[59] as well as PEO segment length (n)[55] impacts the extent of surface modification, with hydrophilicity and protein resistance generally the greatest when m = 13 and n = 8.

SMA efficacy may be limited by its ability to restructure to the aqueous interface as well as their tendency to leach from the base polymer during prolonged exposure to water.[44, 45] While the PEO-silane amphiphile [α-$(EtO)_3Si$-$(CH_2)_3$-$ODMS_{13}$-*block*-PEO_8-OCH_3] demonstrated excellent efficacy as a silicone SMA, questions remain regarding its capacity to retain protein resistance during prolonged aqueous exposure. Moreover, the contributions of its diblock architecture and crosslinkable TEOS end group are not understood. Thus, in this work, a series of three PEO-amphiphile SMAs, which varied in terms of architecture and crosslinkability and each with a PEO segment length of m = 13 and 30, were evaluated in silicone (Figure 1). Thus, the previously studied crosslinkable, diblock PEO-silane amphiphile ("*XL diblock, m = 13*") and that with a longer siloxane tether ("*XL diblock, m = 30*") were compared to the non-crosslinkable SMA analogues ("*diblock, m = 13*" and "*diblock, m = 30*") (i.e. no TEOS group). Additionally, triblock SMA analogues were also evaluated ("*triblock, m = 13*" and "*triblock, m = 30*"). For these triblock SMAs, they are not only non-crosslinkable but contain twice the PEO content as the diblock type SMAs. The increase of the siloxane tether length (m) was hypothesized to increase the affinity of the SMA to the silicone to potentially reduce leaching and potentially diminish the need for covalent crosslinking (i.e. TEOS end group). For each SMA modified silicone, the water-driven surface hydrophilicity and resistance to fibrinogen adsorption were measured before and during prolonged water conditioning. In addition, water uptake and leaching from modified silicones were also measured.

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2. Materials and methods

2.1 Materials

Allyl methyl PEO [Polyglykol AM 450, M_n = 292–644 g mol^{-1} per manufacturer's specifications; M_n = 424 g mol^{-1} per ^{1}H NMR end group analysis; ^{1}H NMR (δ, ppm): 3.35 (s, 3H, OCH_3), 3.51–3.66 (m, 32H, OCH_2CH_2), 4.00 (d, J = 5.4 Hz, 2H, CH_2=$CHCH_2O$), 5.13–5.28 (m, 2H, CH_2=$CHCH_2O$) and 5.82–5.96 (m, 1H, CH_2=$CHCH_2O$)] was kindly provided by Clariant. Octamethylcyclotetrasiloxane, tetramethyldisiloxane, vinyltriethoxysilane (VTEOS), Pt-divinyltetramethyldisiloxane complex (Karstedt's catalyst) in xylene, and α,ω-bis-(SiH)oligodimethylsiloxane$_{13}$ [$ODMS_{13}$; M_n = 1000–1100 g mol^{-1} per manufacturer's specifications; M_n = 1096 g mol^{-1} per ^{1}H NMR end group analysis; ^{1}H NMR (δ, ppm): 0.05–0.10 (m, 78H, $SiCH_3$), 0.19 (d, J = 2.7 Hz, 12H, $OSi[CH_3]_2H$) and 4.67–4.73 (m, 2H, SiH)] were purchased from Gelest. $ODMS_{30}$ [M_n = 2354 g mol^{-1} per ^{1}H NMR end group analysis] was prepared as reported;[1]H NMR (δ, ppm): 0.05–0.11 (m, 180H, $SiCH_3$), 0.19 (d, J = 2.7 Hz, 12H, $OSi[CH_3]_2H$) and 4.67–4.73 (m, 2H, SiH).[60] Triflic acid, $RhCl(Ph_3P)_3$ (Wilkinson's catalyst), hexamethyldisilazane (HMDS), and solvents were obtained from Sigma-Aldrich. All solvents were dried over 4Å molecular sieves prior to use for hydrosilylation reactions and film casting. Glass microscope slides (75 × 25 × 1 mm) were purchased from Fisher Scientific. Medical-grade condensation-cure room-temperature-vulcanizing (RTV) silicone elastomer (MED-1137) was purchased from NuSil Technology. Per manufacturer's specifications, MED-1137 is comprised of α,ω-bis(Si-OH)PDMS, silica (11–21%), methyltriacetoxysilane (<5%), ethyltriacetoxysilane (<5%) and trace amounts of acetic acid. Polystyrene 24-well well plates were purchased from Corning. Human fibrinogen (HF) was purchased from Calbiochem. Tris buffered saline with Tween 20 (TBS-T20), goat anti-fibrinogen horse radish peroxidase (HRP)-conjugated polyclonal detection antibody, and ultra 3,3',5,5'-tetramethylbenzidine dihydrochloride (TMB di-HCl) substrate solution were purchased from Thermo Fisher Scientific.

2.2 Synthetic approach

Reactions were all run under a N_2 atmosphere with a Teflon-covered stir bar. Chemical structures were confirmed with nuclear magnetic resonance (NMR) spectroscopy using a Mercury 300 MHz spectrometer operating in the Fourier transform (FT) mode and using $CDCl_3$ as the standard.

2.2.1. Synthesis of crosslinkable, diblock amphiphile ("XL diblock, m = 13", "XL diblock, m = 30")—Crosslinkable (i.e. "XL") diblock amphiphiles were synthesized as previously reported using a two-step hydrosilylation protocol.[53, 60] Briefly, the $ODMS_m$ (m = 13 or 30) underwent Wilkinson's-catalyzed regioselective hydrosilylation with vinyltriethoxysilane (1:1 molar ratio). Next, each product was reacted with allyl methyl PEO_8 (1:1 molar ratio) via a Karstedt's-catalyzed hydrosilylation reaction.

2.2.2 Synthesis of non-crosslinkable, diblock amphiphiles ("diblock, m = 13", "diblock, m = 30")—Non-crosslinkable diblock amphiphiles (m = 13 and 30) (i.e. lacking a TEOS terminal group) were prepared using a Wilkinson's-catalyzed regioselective hydrosilylation procedure. Allyl methyl PEO_8 and $ODMS_m$ (1:1 molar ratio) were dissolved

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in toluene in a sealed round bottom (rb) flask with Wilkinson's catalyst (10 mg) and heated to 80 °C. After 16 h, the catalyst was removed from the reaction mixture by adding activated charcoal and heating at 90 °C for 2 h. The mixture was then cooled to room temperature (RT) and filtered to remove the charcoal. After filtration, the volatiles were removed under reduced pressure to yield a colorless liquid.

"Diblock, m = 13".: Allyl methyl PEO_8 (3.09 g, 7.29 mmol) and $ODMS_{13}$ (8.00 g, 7.30 mmol) and Wilkinson's catalyst were reacted in 50 mL toluene to yield the product (8.98 g, 81% yield). ^{1}H NMR (δ, ppm): 0.04–0.10 (m, 84H, SiCH_3), 0.18–0.19 (d, J = 2.7 Hz, 6H, OSi[CH_3]$_2$H), 0.48–0.54 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.55–1.66 (m, 2H, SiCH$_2$CH_2CH$_2$), 3.37 (s, 3H, OCH_3), 3.38–3.43 (t, J = 7.1 Hz, 2H, SiCH$_2$CH$_2$CH_2), 3.53–3.71 (m, 32H, CH_2CH_2O), and 4.67–4.73 (m, 1H, SiH).

"Diblock, m = 30".: Allyl methyl PEO_8 (2.48 g, 5.85 mmol) and $ODMS_{30}$ (13.79 g, 5.86 mmol) and Wilkinson's catalyst were reacted in 50 mL toluene to yield the product (13.00 g, 80% yield). ^{1}H NMR (δ, ppm): 0.05–0.10 (m, 186H, SiCH_3), 0.18–0.19 (d, J = 2.7 Hz, 6H, OSi[CH_3]$_2$H), 0.45–0.54 (m, 2H, SiCH_2CH$_2$CH$_2$), 1.55–1.66 (m, 2H, SiCH$_2$CH_2CH$_2$), 3.37 (s, 3H, OCH_3), 3.38–3.43 (t, J = 7.4 Hz, 2H, SiCH$_2$CH$_2$CH_2), 3.53–3.66 (m, 32H, CH_2CH_2O), and 4.67–4.73 (m, 1H, SiH).

2.2.3 Synthesis of non-crosslinkable, triblock amphiphiles ("triblock, m = 13", "triblock, m = 30")—

Non-crosslinkable triblock amphiphiles (m = 13 and 30) (i.e. no TEOS group) were prepared using a Karstedt's-catalyzed hydrosilylation procedure. Allyl methyl PEO_8 and $ODMS_m$ (2:1 molar ratio) were dissolved in toluene in a sealed rb flask with Karstedt's catalyst and heated to 80 °C. After 16 h, the catalyst was removed by adding activated charcoal to the reaction mixture and heating at 90 °C for 2 h. The mixture was then cooled to RT and filtered. The volatiles were then removed under reduced pressure to yield the colorless liquid.

"Triblock, m = 13".: Allyl methyl PEO_8 (3.21 g, 7.57 mmol) and $ODMS_{13}$ (4.15 g, 3.79 mmol) and Karstedt's catalyst (25 μL) were reacted in 30 mL toluene to yield the product (3.35 g, 46% yield). ^{1}H NMR (δ, ppm): 0.04–0.09 (m, 90H, SiCH_3), 0.48–0.54 (m, 4H, SiCH_2CH$_2$CH$_2$), 1.55–1.66 (m, 4H, SiCH$_2$CH_2CH$_2$), 3.37 (s, 6H, OCH_3), 3.37 (t, J = 7.1 Hz, 4H, SiCH$_2$CH$_2$CH_2), and 3.53–3.71 (m, 64H, CH_2CH_2O).

"Triblock, m = 30".: Allyl methyl PEO_8 (1.49 g, 3.51 mmol) and $ODMS_{30}$ (4.12 g, 1.75 mmol) and Karstedt's catalyst (25 μL) were reacted in 30 mL toluene to yield the product (3.67 g, 65% yield). ^{1}H NMR (δ, ppm): 0.05–0.09 (m, 192H, SiCH_3), 0.48–0.54 (m, 4H, SiCH_2CH$_2$CH$_2$), 1.55–1.67 (m, 4H, SiCH$_2$CH_2CH$_2$), 3.37 (s, 6H, OCH_3), 3.37–3.43 (t, J = 7.1 Hz, 4H, SiCH$_2$CH$_2$CH_2), and 3.53–3.71 (m, 64H, CH_2CH_2O).

2.3 Film preparation

Glass microscope slides were sequentially rinsed with dichloromethane (DCM) and acetone followed by drying in a 120 °C oven overnight. Casting solutions were prepared by combining MED-1137 with hexane (1:3 wt/wt) and mixing with a vortexer until a

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homogenous solution was obtained. For modification of silicone, each SMA amphiphile was added to individual casting solutions at 50 μmol of SMA per 1 g of silicone. Solutions were solvent-cast onto leveled glass slides (1.5 mL per slide; 2.0 mL for leaching study) and covered with a Petri dish. For protein testing, solutions were solvent-cast into 24-well plates (0.25 mL per well). All films were allowed to cure for one week at RT and then promptly used for designated analyses.

2.4 Water-driven surface restructuring

Water-driven surface restructuring of silicones was characterized with static water contact angle (θ_{static}) measurements using a CAM-200 goniometer (KSV Instruments) equipped with an autodispenser, video camera, and drop-shape analysis software (Attension Theta). "Non-conditioned" films (i.e. not conditioned in water) were measured immediately after one week of curing. A 5 μL deionized (DI) water droplet was placed on the film and θ_{static} was iteratively measured over a 5 min period. The reported θ_{static} values are an average and standard deviation of three measurements each made on different areas of the same film. An equivalent set of films were subjected to conditioning in DI water and subsequent contact angle measurement. For these, a coated glass slide was sequentially submerged in ~30 mL of fresh DI water in plastic Petri dish, removed after a given time period (t = 2 h, 6 h, 24 h, 48 h, 72 h, 6 days, 10 days, and 14 days), quickly dried under a stream of nitrogen and $\theta_{static, 5\ min}$ measured as above. On the 14th day, each conditioned film was dried under reduced pressure overnight (30 in. Hg, 50 °C) and $\theta_{static, 5\ min}$ was measured.

2.5 Water uptake

Triplicate films were prepared and subsequently submerged in 30 mL DI water in plastic Petri dishes. After 24 h, 7 days and 14 days, the films were removed from water and briefly dried with stream of air and blotted with a paper towel. The water content of the film was measured by thermal gravimetric analysis (TGA). A 20 ± 2 mg segment of film was removed from the glass slide by razor blade and placed in a platinum TGA pan. Using a TA Instruments Q50, weight loss was measured as the sample was heated from RT to 150 °C at a rate of 10 °C min^{-1}. Water loss was observed as a peak in the mass loss derivative curve that occurred between RT and approximately 100 °C. Wt% water content of each film was then determined by measuring the percent mass loss over the bounds of that peak. After each measurement, the films were re-submerged in fresh DI water to advance to the next time period. The reported values are the average water contents and standard deviation of three identically-prepared films at the same submersion time.

2.6 Water-induced mass loss

Coated slides were weighed (W_i) and then each soaked in DI water (30 mL) at RT for two weeks. The coated slides were subsequently dried at RT under reduced pressure (30 in. Hg) and weighed (W_f). The weight of the uncoated glass slide was subtracted from W_i and W_f before calculating the water-induced mass loss (i.e. water-extractable content). Measurements were performed on triplicate films. Mass loss is defined as:

$$\text{Water-induced mass loss } (\%) = \left[\left(W_i - W_f\right)/Wi\right] \text{ x } 100 \qquad \text{(Equation 1)}$$

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2.7 Protein adsorption

Human fibrinogen (HF) adsorption was measured using a modified immunosorbent assay.[61] Three replicate coated wells of each composition were exposed to 0.15 mL of HF solution prepared in phosphate buffered saline (PBS) (3.0 mg/mL) and statically incubated for 1 h at 37 °C. The protein solution was removed and each well was rinsed three times with PBS before the addition of TBS-T20 (0.50 mL), which was incubated for 30 min at 37 °C. Wells were then rinsed three times with TBS-T20. Next, to each well was added 0.5 mL goat anti-fibrinogen (HRP)-conjugated polyclonal detection antibody (1:50,000 dilution in TBS-T20) and statically incubated for 1 h at 37 °C. Wells were then rinsed three times with TBS-T20. TMB di-HCl substrate solution (0.5 mL) was added and allowed to incubate for 30 min at 37 °C. To stop the reaction, 2 M H_2SO_4 was added to each well and plates were shaken on an orbital shaker at RT for 15 min. To quantify the amount of adsorbed HF on each surface, 0.15 mL of each resulting solution was transferred to a 96-well plate, absorbance was measured at 450 nm using a spectrophotometer (Tecan Safire^2), and the value was compared to a HF standard curve (0.01 to 1000 ng/mL).

3. Results and discussion

3.1 Water-driven surface restructuring: before, during, and after conditioning in water

The efficacy of amphiphiles as SMAs to improve silicone protein resistance is predicted to be governed by their ability to undergo water-driven surface reorganization to form a hydrophilic, PEO-enriched surface. Previously, this process was directly observed for silicones modified with "*XL diblock, m = 13*".[53–55] The temporal measurement of the decrease in water droplet θ_{static} values was utilized to monitor the relative rate and extent of PEO migration to the silicone surface-water interface. Thus, the θ_{static} values of water droplets deposited onto surfaces were measured over a 5 min period (Figure 2, Table S1). While the unmodified silicone expectedly remained very hydrophobic (θ_{static} = ~106 °), all SMA modified silicones exhibited initially similar hydrophobicity but rapidly underwent significant water-driven restructuring to form very hydrophilic surfaces. Temporal θ_{static} value profiles were dependent on SMA structure, including the siloxane tether length. For instance, for silicones modified with "*XL diblock, m =13*" and "*triblock, m =13*", $\theta_{static,\ 5\ min}$ values were somewhat similar to those of silicones modified with the corresponding SMA of greater siloxane tether length (m = 30). In contrast, "*diblock, m = 13*" ($\theta_{static,\ 5\ min}$ = ~6 °) produced a modified silicone of significantly greater hydrophilicity versus "*diblock, m = 30"* ($\theta_{static,\ 5\ min}$ = ~26 °) as well as "*XL diblock, m = 13*" ($\theta_{static,\ 5\ min}$ = ~28 °) and "*triblock, n =13*" ($\theta_{static,\ 5\ min}$ = ~21°). The enhanced water-driven surface migration potential of "*diblock, m = 13*" versus "*XL diblock, m = 13*" is attributed to the former's greater chain mobility, being not limited by covalent attachment to the silicone network. Despite the similar lack of crosslinking, "*diblock, m = 30*" appeared to be more limited in its surface migration potential versus "*diblock, m = 13*", perhaps due to the longer siloxane tethers' higher affinity of the silicone matrix and increased steric constraints. Notably, while "*triblock, m = 13*" contained twice the amount of PEO, it produced lesser hydrophilicity versus "*diblock, m = 13*". This reduced migration potential may also be due to steric constraints of an overall higher molecular weight triblock chain.

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Critical to their sustained anti-fouling behavior is the capacity of modified silicones containing SMAs to retain their surface hydrophilicity during prolonged exposure to water. Thus, over a two-week conditioning period in DI water, $\theta_{\text{static, 5 min}}$ values were periodically measured (Figure 3, Table S2). Interestingly, after two weeks, all modified silicones exhibited similar hydrophilicity, having $\theta_{\text{static, 5 min}}$ values between ~36 and 43 °. However, these $\theta_{\text{static, 5 min}}$ values were somewhat higher than at t = 0, indicating migration of PEO away from the water-interface. Versus prior to conditioning in water (i.e. "t = 0 h"), modified silicones exhibited a modest increase in $\theta_{\text{static, 5 min}}$ of at least ~8 ° by two weeks. The lowest increase in $\Delta\theta_{\text{static, 5 min}}$ was observed for the silicone modified with "*XL diblock, m = 30*" (~8 ° increase) whereas the highest increase was observed with "*diblock, m = 13*" (~30 ° increase). The silicone modified with "*diblock, = 30*" exhibited a modest increase (~15 °), much lower than for "*diblock, m = 13*" and similar to that for silicone modified with "*XL diblock, m = 13*". Intermediate water uptake values were observed for silicones modified with triblock SMAs. Based on these results, stability of surface hydrophilicity during water exposure is best for silicones modified with diblock SMA having a crosslinkable group and a longer siloxane tether (m = 30). However, the crosslinkable group may be eliminated without large reductions in surface hydrophilicity for diblock SMAs with the longer siloxane tether (m = 30).

As noted, during conditioning, water absorption by modified silicones may contribute to their decreased hydrophilicity by inducing migration of the PEO from the water-interface and back into the bulk. If this is the case, subsequent drying of water conditioned specimens should restore the surface hydrophilicity to that initially observed (i.e. $\theta_{\text{static, 5 min}}$ at t = 0). Thus, after two weeks of conditioning in water, the specimens were subsequently dried (36 mm Hg, 50 °C, overnight) and $\theta_{\text{static, 5 min}}$ measured (Figure 3, Table S2). Indeed, following drying, most modified silicones exhibited $\theta_{\text{static, 5 min}}$ values similar that at t = 0. The only exception was silicone modified with "*diblock, m = 13*" whose $\theta_{\text{static, 5 min}}$ was ~20 ° after drying compared to ~6 ° before water conditioning (t = 0). As noted above, this modified silicone experienced the highest increase in $\Delta\theta_{\text{static, 5 min}}$ following exposure to water. Its irreversible change in surface hydrophilicity was considered to possibly be indicative of leaching from the silicone and is considered below. Overall, however, water uptake into the films contributed to the observed decrease in hydrophilicity upon prolonged exposure to water. Still, following two weeks of water conditioning, all modified silicones remained quite hydrophilic.

3.2 Water uptake

As noted above, water uptake contributed to the decrease in surface hydrophilicity of modified silicones. Thus, the amount of water absorbed by each modified silicone was quantified when conditioned in water for 24 h, one week and two weeks (Figure 4, Table S3). The unmodified silicone expectedly absorbed little water (<0.1 wt%) due to its hydrophobicity. After just 24 h of conditioning, silicones modified with SMA amphiphiles absorbed more water (between ~0.8 and ~2.8 wt%) due to their greater hydrophilicity imparted by PEO. Given the ability of block copolymers to undergo local aggregation within polymer matrixes,[62] these SMA amphiphiles are hypothesized to form micelle-like structures in the silicone to contain the absorbed water. Water uptake into modified silicones

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increased from 24 h to one week of conditioning, but did not increase substantially at two weeks. Final wt% water values of modified silicones depending on SMA structure and ranged modified from ~1.6 – 6 wt%. SMAs with a longer siloxane tether reduced water absorption, even when not crosslinkable. In this way, the least amount of water adsorbed (< 2 wt%) at two weeks was observed for the silicone modified with "*XL diblock, m = 30*" and "*diblock, m = 30*". For diblock SMAs with the shorter siloxane tether (*m* = 13), a lack of crosslinkability led to higher water adsorption ("*XL diblock, m = 13*"; ~3% and "*diblock, m = 13*"; ~6 %). Due to it increased PEO content, the silicone modified with "*triblock, m = 30"* produced a modified silicone with higher water absorption (~6 wt%). Thus, diblock SMAs having a longer siloxane tether, even in the absence of a crosslinkable group, are the most efficient at reducing water uptake into modified silicones.

3.3 Water-induced mass loss

During exposure to water, mass loss measurements following two weeks of exposure to DI water was used to determine if significant mass loss occurred which could indicate leaching of the SMA amphiphile from the modified silicone. For the unmodified silicone control, a ~0.7 wt% mass loss was observed (Figure 5, Table S4). For modified silicones, wt% mass loss increased only slightly, to ~0.9 – 1.4 wt%. Also, while all SMA amphiphiles were added at 50 μmol to silicones, the corresponding wt% values are appreciably higher than the wt% loss following conditioning in water. As noted above and in Figure 3, initial surface hydrophilicity (i.e. $\theta_{\text{static, 5 min}}$ at t = 0) was recovered when modified silicones which were dried following conditioning in water. The only exception was for the silicone modified with "*diblock, m = 13*". However, since a substantial increase in weight loss was not observed, leaching of the "*diblock, m = 13*" cannot be the source of this observation. We speculate that this modified silicone may have retained some residual water during drying, reducing its recovery of initial surface hydrophilicity.

3.4 Protein adsorption

The adsorption of HF protein on modified silicones was evaluated before and after two weeks of conditioning in water (Figure 6, Table S5). As expected, unmodified silicone films, due to their hydrophobicity, adsorbed a relatively large amount of HF before and after water conditioning (~125 and ~138 ng cm^{-2}, respectively). For all silicones modified with SMA amphiphiles, protein resistance was very high at t = 0 and adsorbed HF concentrations were dramatically reduced to ~2 – 12 ng cm^{-2}. As noted above, conditioning of modified silicones in water for two weeks led to a reduction in surface hydrophilicity (i.e. increased $\theta_{\text{static, 5 min}}$) (Figure 3, Table S2). Thus, the impact of water conditioning on modified silicones' resistance to HF was assessed by also measuring protein adsorption immediately following two weeks of aqueous exposure. Modified silicones exhibited either similar or a very minor increase in HF adsorption following water conditioning. The one exception was for the silicone modified with "*triblock, m =30*" which exhibited a substantial increase in HF adsorption (~74 ng cm^{-2}). For the silicone modified with this triblock SMA, surface hydrophilicity after two weeks of conditioning was not significantly different versus silicones modified with other amphiphiles (Figure 3), nor did this silicone show any evidence of amphiphile leaching (Figure 5). Thus, while it is not expected that surface hydrophilicity (i.e. $\theta_{\text{static, 5 min}}$) and protein adsorption correlate in a scalable fashion, this

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result does highlight that other factors influence protein resistance. In total, the ability of diblock SMAs, with or without crosslinking, to maintain protein resistance following water conditioning is notable.

4. Conclusion

Silicones, due to their extreme hydrophobicity, exhibit poor anti-fouling behavior which limits their efficacy in medical devices as well as for non-toxic marine coatings. PEO-based SMAs represent a potentially convenient way to modify silicones to impart migration of PEO to the aqueous (i.e. biological) interface resulting in increased surface hydrophilicity and a reduction in protein adsorption and other biofouling processes. By reducing protein adsorption and biofouling of silicones, PEO-based SMAs can allow for safe, effective, and non-toxic silicones for medical devices and environmentally friendly marine coatings. Previously, we have described a PEO-silane amphiphile SMAs having a diblock architecture and being comprise of a siloxane tether and crosslinkable TEOS group [α-$(EtO)_3$Si-$(CH_2)_3$-$ODMS_{13}$-*block*-PEO_8-OCH_3] ("*XL diblock, m = 13*"). When used to bulk modify RTV silicones, exposure to water led to a rapid and dramatic increase in surface hydrophilicity due to migration of PEO to the water interface and a substantial reduction in biofouling. In contrast, conventional PEO-silanes [$(EtO)_3$Si-$(CH_2)_3$-PEO_8-OCH_3] acted as a poor SMAs in silicones. Given the effectiveness of the PEO-silane amphiphile as a SMA, this work sought to identify whether such modified silicones would retain their anti-fouling behavior during prolonged exposure to water. Additionally, the contributions of its diblock architecture and crosslinkable TEOS end group were examined by comparing to non-crosslinkable diblock and triblock analogues. Given its affinity to the silicone matrix, the length of the siloxane tether (*m*) was also increased to 30. Thus, a series of six PEO-based amphiphile SMAs, which varied in terms of architecture and crosslinkability and each with a siloxane tether length of *m* = 13 and 30, were evaluated in silicone: crosslinkable, diblock SMAs ("*XL diblock, m = 13*" and "*XL diblock, m = 30*"), non-crosslinkable, diblock SMAs ("*diblock, m = 13*" and "*diblock, m = 30*") and non-crosslinkable, triblock SMAs ("*triblock, m = 13*" and "*triblock, m = 30*"). After just 5 minutes of aqueous exposure, while all modified silicones were very hydrophilic, the silicone modified with "*diblock, m = 13*" was the most hydrophilic (i.e. lowest $\theta_{\text{static, 5 min}}$). However, following two weeks of aqueous conditioning, all modified silicones exhibited rather similar surface hydrophilicity. After subsequent drying of these water conditioned silicones, most were able to achieve their original surface hydrophilicity (i.e. $\theta_{\text{static, 5 min}}$ at t = 0) with the exception to the silicone modified with "*diblock, m = 13*". Among modified silicones, water uptake was lowest and similar for those prepared with diblock SMAs having longer siloxane tethers ("XL *diblock, m = 30*" and "*diblock, m = 30*"). Leaching studies confirmed that, even for the silicone modified with "*diblock, m =13*", SMAs were not lost at appreciable levels (between ~0.9 and 1.4 wt%). Adsorption of fibrinogen protein before and after two weeks of water conditioning remained very low with the exception of "*triblock, m = 30*". These studies confirm that a diblock architecture is more effective versus triblock for these SMA amphiphiles, despite twice the PEO content in triblock SMAs. Reducing the decrease in surface hydrophilicity during water conditioning and minimizing water uptake as well as leaching was best controlled for diblock SMAs when the siloxane tether length is increased

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from $m = 13$ to $m = 30$. Moreover, the need for a TEOS crosslinking group is no longer necessary as the longer siloxane tether's affinity to the silicone is enhanced. These results will be useful for the modification of silicones with PEO-based SMAs for the reduction of biofouling.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

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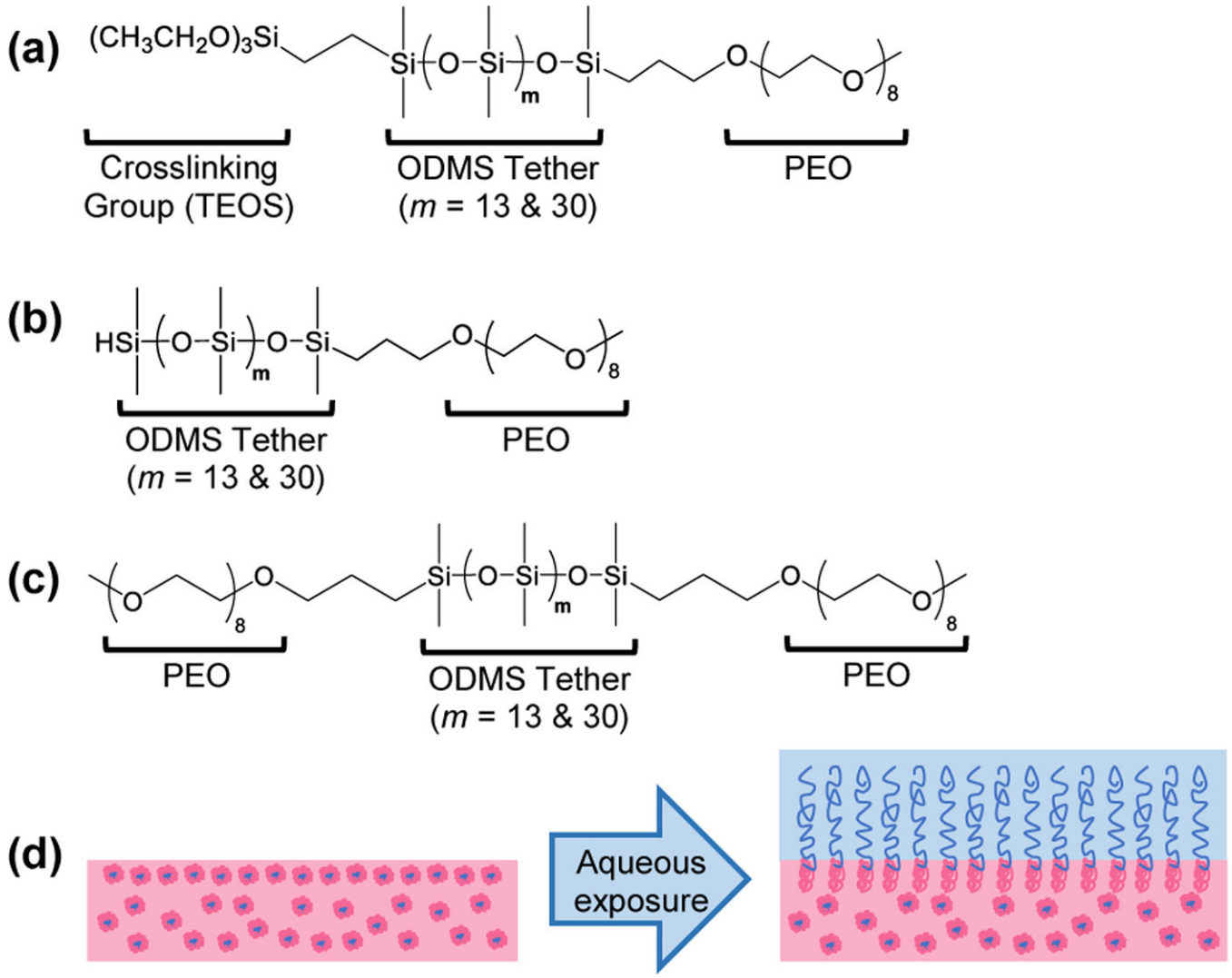

Figure 1.

Surface-modifying additive (SMA) amphiphile structures: (a) “XL diblock amphiphile”, (b) “diblock amphiphile”, and (c) “triblock amphiphile”. (d) Upon aqueous exposure, silicones modified with these amphiphilic SMAs can undergo rapid, water-driven surface restructuring to present PEO chains to the surface and form a hydrophilic, protein resistant surface. The image shown represents restructuring of the “XL diblock” and “diblock” SMAs.

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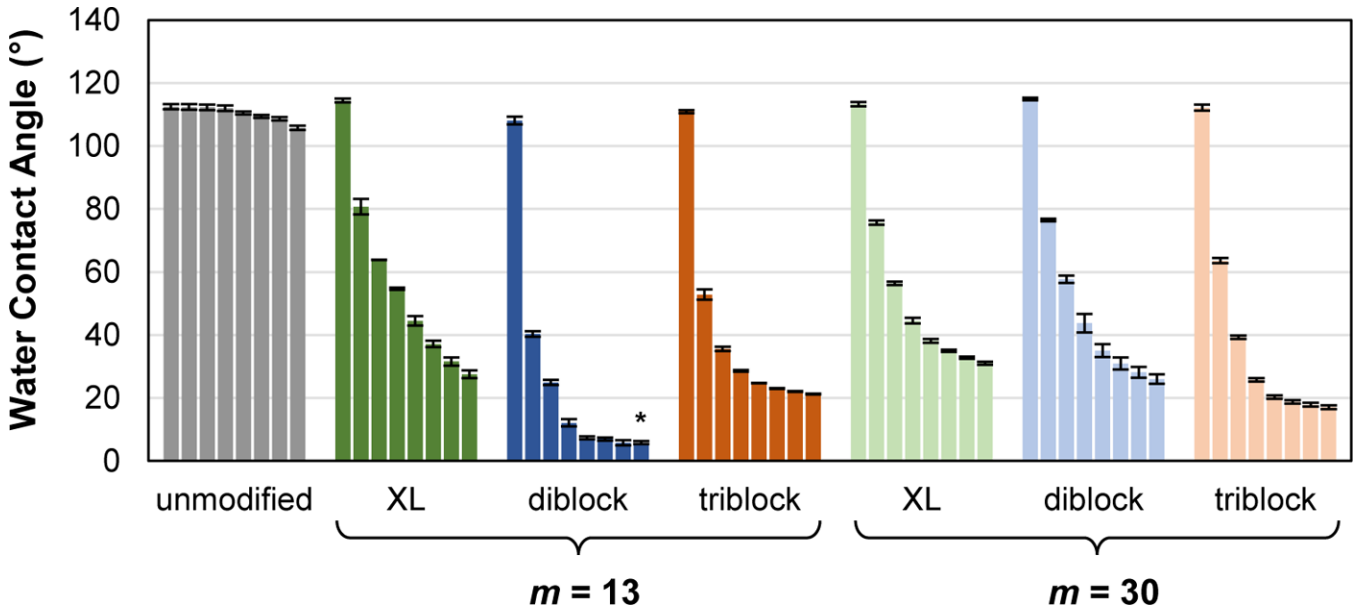

Figure 2.

Following one-week cure, θ_{static} measured over a 5 min period on silicones bulk-modified with SMA amphiphiles ("XL diblock", "diblock" and "triblock"; m = 13 and 30 for each). Bars are organized as time after the initial drop placement from left to right as follows: 0 s, 15 s, 30 s, 1 min, 2 min, 3 min, 4 min, and 5 min. Statistical analysis was done using single factor Anova. The "diblock, m = 13" (t = 5 min) was compared against all other compositions at t = 5 min (* indicates $p < 0.01$).

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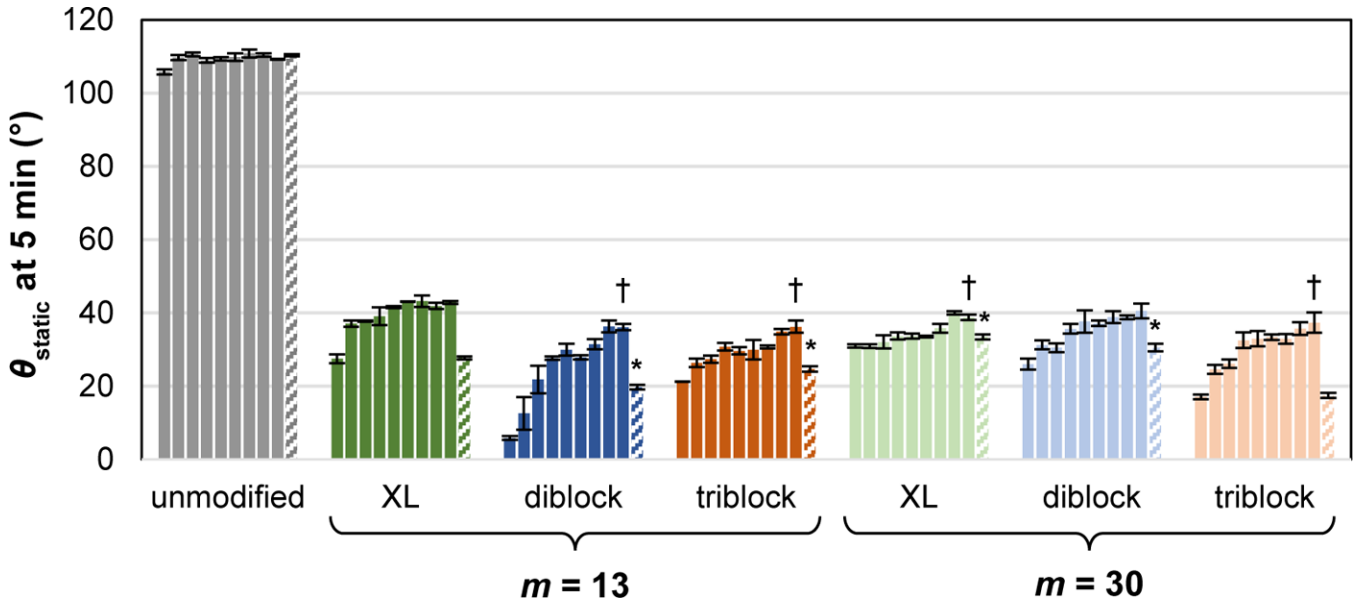

Figure 3.

During a two-week exposure to DI water, θ_{static} was measured over a 5 min period on silicones bulk-modified with SMA amphiphiles ("XL diblock", "diblock" and "triblock"; m = 13 and 30 for each). Bars are organized in terms of time of duration of water conditioning from left to right: 0 h, 2 h, 6 h, 24 h, 48 h, 72 h, 6 days, 10 days, and 14 days. The final "patterned bar" in each series represents $\theta_{static,\ 5\ min}$ following drying of the "14 day" water-conditioned specimens. (Note: 0 h time point corresponds to 5 min θ_{static} value in Figure 2.) Statistical analysis was done using single factor Anova. First, the t = 0 h time point was compared to the final "patterned bar" in each series (*indicates $p < 0.05$). Second, the t = 14 day time point of each SMA were compared to the t = 14 day time point of "*XL diblock, m = 13*" († indicates $p < 0.05$).

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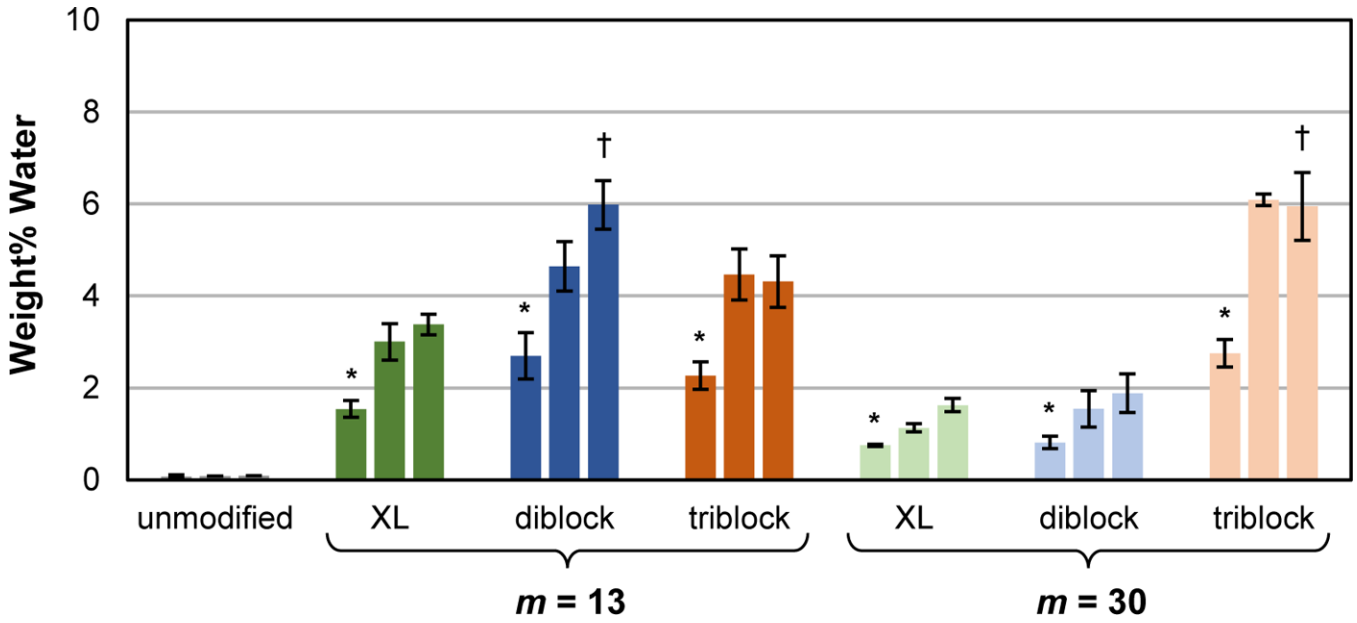

Figure 4.

Wt% water absorbed by silicones modified with SMA amphiphiles ("XL diblock", "diblock" and "triblock"; $m = 13$ and 30 for each). Bars are organized in terms of duration of water conditioning from left to right: 1 day, 1 week, and 2 weeks. Statistical analysis was done using single factor Anova. First, following 24 h of conditioning, wt% water absorbed by modified silicones were compared against the unmodified silicone control (* indicates $p < 0.05$). Second, following 2 weeks of conditioning, wt% water absorbed by silicones modified with a given SMA ($m = 13$) were compared to that modified with the corresponding SMA ($m = 30$) († indicates $p < 0.05$).

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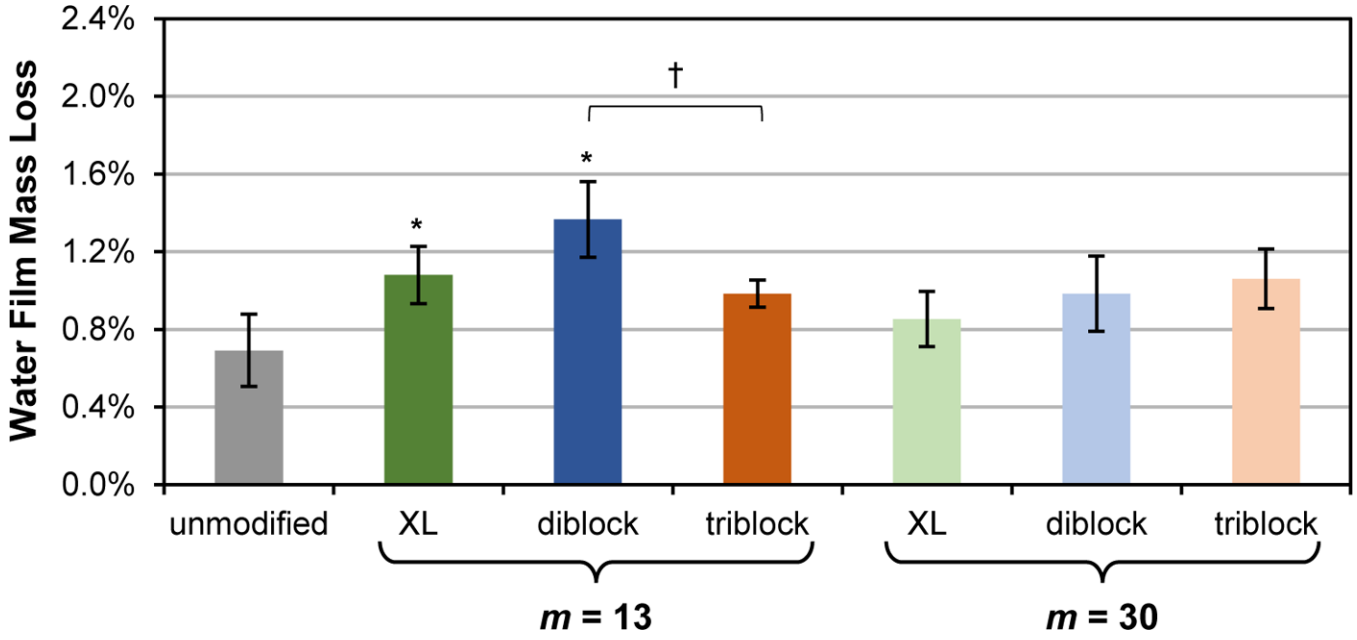

Figure 5.

Following exposure to water for 2 weeks, wt% mass loss from silicones modified with SMA amphiphiles ("XL diblock", "diblock" and "triblock"; m = 13 and 30 for each). Each bar represents an average percent mass loss of three identically prepared films with the error bar representing the standard deviation. Statistical analysis was done using single factor Anova. Mass loss of bulk-modified films were compared against the unmodified control (* indicates $p < 0.05$). Mass loss of bulk-modified films within a tether length series (m = 13 or m = 30) were also compared († indicates $p < 0.05$).

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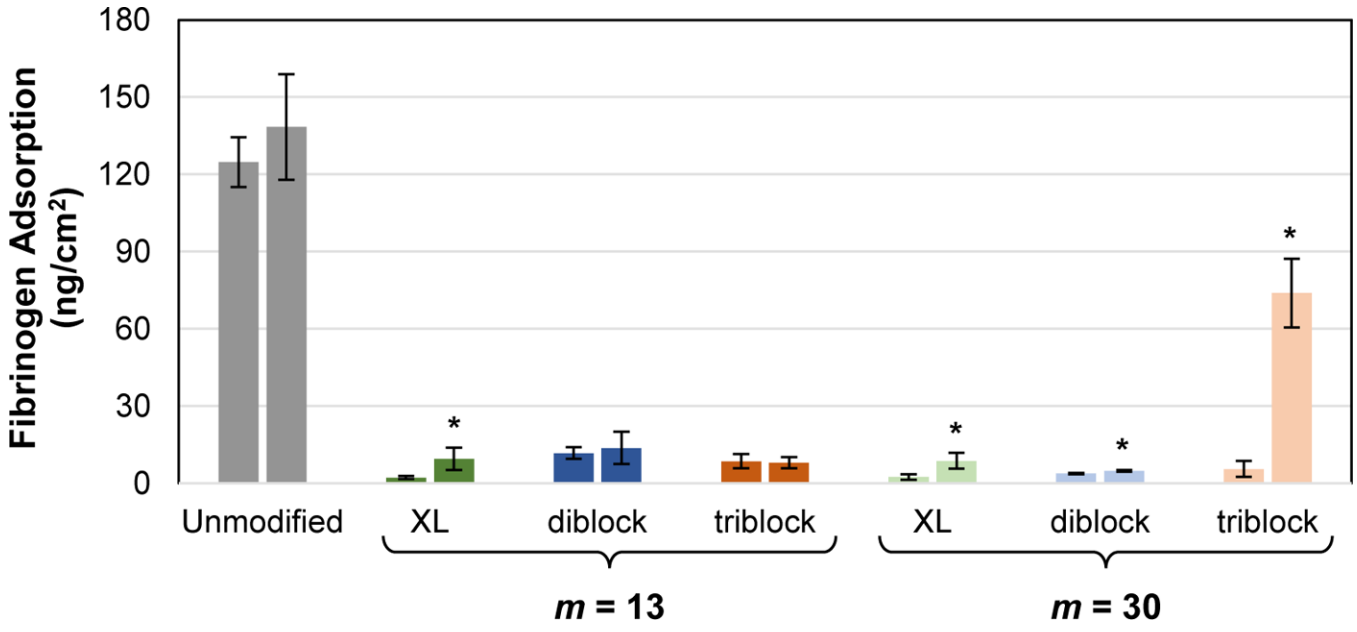

Figure 6.

Fibrinogen adsorption (concentration = 3 mg/mL; exposure time = 1 h) onto silicones modified with SMA amphiphiles ("XL diblock", "diblock" and "triblock"; $m = 13$ and 30 for each) before (t = 0) and after 2 weeks exposure to water (t = 2 weeks). For each composition fibrinogen adsorption was measured before and after water-equilibration as represented by the left and right bars, respectively. Each individual bar represents the average fibrinogen adsorption of three identically prepared replicate wells with the error bars representing the standard deviations. Statistical analysis was done using single factor Anova. Fibrinogen adsorption values were compared at t = 0 versus t = 2 weeks (* indicates $p < 0.05$).