

**STABILITY ASSESSMENT OF PEO-SILANE AMPHIPHILES FOR USE
IN INTRAOCULAR LENSES**

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Stability Assessment of PEO-Silane Amphiphiles for Use in Intraocular Lenses

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Surface modifying additives (SMAs) incorporated into silicones can enhance surface hydrophilicity, thereby achieving resistance to biological adhesion (e.g. proteins). Such anti-biofouling behavior plays a crucial role in proteinaceous fluid-contacting medical devices, including catheters, stents, microfluidics, and ophthalmic implants. Protein adsorption and subsequent cell encroachment is particularly pernicious for intraocular lenses (IOLs), many of which are silicone-based. Therefore, it is essential for IOL silicones modified with SMAs to exhibit surface properties (e.g. hydrophilicity) to control cell on- growth while maintaining adequate bulk mechanical properties, and also optical clarity. Our lab previously developed new poly(ethylene oxide) (PEO)-silane amphiphiles as SMAs for silicones. These were comprised of a PEO segment, an oligodimethylsiloxane tether, and an optional crosslinking group. Silicones based on polydimethylsiloxane (PDMS) were modified with these SMAs, and demonstrated significant improvements in water-driven surface hydrophilicity as well as resistance to bacteria, proteins, and blood. However, for IOLs, a phenyl-containing silicone is most frequently utilized. Thus, this project aimed to evaluate the utility of PEO-silane amphiphile SMAs with a medical grade phenyl

silicone material. The SMA was incorporated at varying concentrations. In addition to the assessment of water-driven surface hydrophilicity, the stability of these modified phenyl silicones during continuous exposure to air and to water was evaluated. The bulk mechanical properties as well as optical properties were also assessed.

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1. INTRODUCTION

Certain types of medical devices must be implanted inside the body to assist or repair a specific physiologic function. When a polymeric material enters the aqueous environment of the human body, different ions, water, and proteins adsorb to its surface. The extent of protein adsorption to the material is largely dependent on the properties of the surface including roughness, charge, and – most importantly for this project – hydrophilicity. Materials exhibiting hydrophobic surfaces are more likely to experience high levels of protein adsorption after implantation, triggering cell-on-growth and an immune response against the implant.¹ The extent of this host response can ultimately hinder the implant’s functionality and lead to its failure.

Cell encroachment is particularly pernicious for intraocular lenses (IOLs). IOLs are medical devices which replace the natural lens of the eye after it has been surgically removed as a treatment of cataracts. According to the World Health Organization (WHO), cataracts severely impair the vision in 94 million people worldwide. Although IOLs can restore vision after surgery, a condition known as posterior capsule opacification (PCO) develops as a result of extensive lens epithelial cell growth on the surface of the IOL.² PCO may occur just months after surgery in up to 50% of people undergoing IOL implantations, leading to significant light scatter and obscuring of the visual axis which may ultimately cause the removal of the IOL.³ The extent of cell encroachment can be attributed to the hydrophobic nature of materials like acrylics and silicones, which make up a majority of lenses.⁴

A current approach to correct PCO in IOLs is posterior capsulotomy with a Neodymium:YAG (Nd:YAG) surgical laser procedure. However, there are several risks associated with this treatment, including glaucoma and retinal detachment.⁵ To address this issue, current lens

material modification approaches utilize complicated surface deposition of biomolecules like heparin, or modifications to the bulk design of the IOL (e.g. changing round corners to sharp edges). Although these techniques offer promising results, their limitations include lack of long-term stability and the introduction of unwanted glare effects.⁶ Therefore, in biomedical applications, it is exceptionally important to develop techniques to modify the surface chemistry of polymeric biomaterials and improve the safety and biocompatibility of medical implants.

Amphiphile behavior has been widely studied for the modification of the surface of silicone biomaterials to tune their surface chemistry. Poly(ethylene oxide) (PEO)-silane amphiphiles, bearing a crosslinkable end-group, an oligodimethylsiloxane tether, and a PEO segment, have been shown to be exceptional surface modifying additives (SMAs) for conventional silicones, rendering them highly resistant to proteins and bacteria.⁷ The PEO segment is hydrophilic and highly flexible while the ODMS tether is hydrophobic.⁸ Our lab has previously demonstrated that, when this amphiphile is incorporated into a silicone material and exposed to aqueous environments, the modified silicones undergo a surface reorganization process in which the PEO segments rapidly migrate to the aqueous interface.⁶ This PEO-rich surface increases the hydrophilicity of the surface-water interface by creating a hydrated PEO layer, and the steric hinderance provided by the PEO chains can also block adhesion sites to proteins, successfully reducing both nonspecific protein adsorption and cell adhesion.⁷

In the past, PEO surface modifications on biomaterials have observed positive results at reducing the adhesion of biomolecules to the surface when tested *in vitro*.⁸ However, *in vivo* tests have demonstrated the opposite with inconsistent results and several instances where such results fail to meet *in vitro* expectations.⁹ Therefore, rather critical for the efficacy of SMAs incorporated into silicones is the physicochemical stability of the surface modification. The ability of these

modifications to retain surface hydrophilicity, without compromising structural integrity and optical clarity, must be evaluated to confirm the potential of these modified silicones for their use in IOLs. Our lab previously demonstrated that PEO-silane amphiphiles used as SMAs initially retained surface hydrophilicity after aqueous exposure.¹⁰ Although both architecture and crosslinking were evaluated as factors of SMA efficacy, these studies were limited to a single concentration of each SMA and were loaded into a condensation cure solvent cast silicone, which is not used to prepare IOLs – indicating that although varying concentration is an important factor in controlling physicochemical properties, its effects on SMA stability have not been thoroughly studied.¹⁰ Therefore, in this project we aim to obtain a detailed assessment of the stability of PEO-silane amphiphiles, as controlled by composition and varying chemical moieties, which is expected to provide thorough and valuable insight into the efficacy of SMAs. Additionally, an *in vitro* aqueous equilibration that closely resembles the physiologic environment of IOLs within the eye, as opposed to simply using water, should reveal important features on stability and the expected performance of these SMAs *in vivo*.

Four different PEO-silane amphiphiles were incorporated into medical grade phenyl silicone films at five different concentrations (0, 5, 10, 15 and 25 $\mu\text{mol/g}$ silicone). To evaluate SMA stability and ensure that the bulk properties of the material remain unchanged after addition of the SMA (i.e. modulus, strength, ductility, and optical clarity), all samples were subjected to tensile and optical tests. All films were fabricated using a medical grade, platinum cure silicone and a PEO-silane amphiphile.

2. MATERIALS AND METHODS

2.1 Materials

UNIOX-PKA 5008 [Allyl methyl PEO (AM PEO8) from NOF Corporation, $M_n = 450$ g mol⁻¹ per manufacturer's specifications; $M_n = 450$ g mol⁻¹ per ¹H NMR end group analysis; ¹H NMR (δ , ppm): 3.37 (s, 3H, OCH₃), 3.53–3.65 (m, 34H, OCH₂CH₂), 3.99–4.02 (d, $J = 5.4$ Hz, 2H, CH₂=CHCH₂O), 5.14–5.29 (m, 2H, CH₂=CHCH₂O) and 5.84–5.96 (m, 1H, CH₂=CHCH₂O)] was provided by Clariant. Tetramethyldisiloxane (TMDS), octamethylcyclotetrasiloxane (D₄), octaphenylcyclotetrasiloxane (D_{4P}), allyloxy(polyethylene oxide) methyl ether [$M_n \sim 350$ g/mol per manufacturer's specifications], and α,ω -bis-(SiH)oligodimethylsiloxane [α,ω -bis-(SiH)ODMS, (ODMS₁₃); $M_n = 1000$ – 1100 g mol⁻¹ per manufacturer's specifications; $M_n = 1096$ g mol⁻¹ per ¹H NMR end group analysis; ¹H NMR (δ , ppm): 0.05–0.10 (m, 78H, SiCH₃), 0.18–0.19 (d, $J = 2.7$ Hz, 12H, OSi[CH₃]₂H) and 4.67–4.73 (m, 2H, SiH)] were purchased from Gelest. Poly (ethylene glycol) dimethyl ether [$M_n \sim 500$ g/mol, contains 100 ppm BHT as stabilizer per manufacturer's specifications], tris (triphenylphosphine)-rhodium(I) chloride (Wilkinson's catalyst), hexamethyldisilazane, triflic acid, and solvents were purchased from Sigma-Aldrich. Solvents were dried in 4 Å molecular sieves prior to use in reactions. ODMS₃₀ [$M_n = 2354$ g mol⁻¹ per ¹H NMR end group analysis; ¹H NMR (δ , ppm): 0.05–0.10 (m, 180H, SiCH₃), 0.18–0.19 (d, $J = 2.7$ Hz, 12H, OSi[CH₃]₂H) and 4.67–4.73 (m, 2H, SiH)] was prepared as reported via ring opening polymerization of TMDS and D₄. Medical-grade, platinum cure silicone elastomer [MED-6020, per manufacturer's specifications, containing diphenyl siloxane, 5-10 % silicic acid (H₄SiO₄), tetraethyl ester, and reaction products with chlorodimethylsilane]

was purchased from Nusil. Phosphate buffered solution (PBS) without calcium and magnesium (pH 7.4) was acquired from Corning.

2.2 Amphiphile Synthesis

2.2.1 Synthesis of PEO-Silane Control

Per prior reports, TMDS was reacted with AM PEO₈ (1:1 molar ratio) via a Wilkinson's-catalyzed, regioselective hydrosilylation reaction (Figure A1).⁹

2.2.2 Synthesis of Hydride-Terminated Dimethyl Siloxane Amphiphile, tether length of 13 or 30 (HDMS, m = 13 or 30)

HDMS was synthesized as previously reported.⁹ Briefly, the ODMS₁₃ tether was used as received from Gelest. The ODMS₃₀ tether was first synthesized using a room-temperature (RT), triflic-acid-catalyzed ring opening polymerization of TMDS and D4. The ODMS_m ($m = 13$ or 30) tether was then reacted with AM PEO₈ (1:1 molar ratio) via a Wilkinson's-catalyzed, regioselective hydrosilylation reaction (Figure A2-A3).

2.3 Film Fabrication

Equal parts of MED-6020 part A and B were added into a FlackTek Inc. speed mixing cup, per manufacturer's specifications. The required amount of PEO-Silane Amphiphile was added to the mixture which was subsequently mixed in a FlackTek Inc. SpeedMixer™ at 3500 rpm for 1 min. Once the sample was removed from the mixer it was carefully poured into a one-sided mold consisting of glass slide backing and PTFE form. The liquid film was then placed into a vacuum oven at room temperature. The vacuum was allowed to pull at 30 inHg (maximum pressure) for 1 min, after which the oven was degassed to 15 inHg before being pulled back to 30 inHg. This was repeated for five more cycles with maximum pressure being held for 2.5, 3.5, 10, 10 and 10 min

respectively. Films were then placed in an oven preheated to 145 °C and allowed to cure for 1 hr, per the manufacturer's specifications.

2.4 Stability Assessment

The assessment was divided into two phases: air equilibration and aqueous equilibration. During the first phase, films were stored in air at room temperature for two weeks. In the aqueous equilibration phase, an equivalent set of films were stored in a PBS solution at 37 °C while shaking at 120 rpm. Following the two-week period for each phase, key physicochemical properties were evaluated as described below.

2.4.1 Water-Driven Surface Restructuring

Water-driven surface restructuring of SMA modified silicones was characterized with static water contact angle (θ_{static}) measurements using a CAM-200 goniometer (KSV instruments) equipped with an auto dispenser, video camera, and drop-shape analysis software (Attention Theta). Images were taken at 15 sec intervals starting at $t = 0$ secs to $t = 120$ sec. Three droplets were placed on each sample to account for surface variation across individual films; five films were tested for each concentration.

2.4.2 Bulk Mechanical Assessment

Tensile tests were run in accordance with ASTM D1708-18 and ASTM D638-14. Briefly, samples were cut into dog bones in accordance with the aforementioned standard. They were then placed into an Instron 6800 Universal Testing System equipped with tensile clamps. Samples were strained at a rate of 13 mm/min in accordance with a break time between 0.5 to 5 min. Young's modulus was determined at 10% strain using a MATLAB algorithm. A minimum of 5 samples were tested to ensure statistical significance of both average measurements and standard deviation.

2.4.3 *Optical properties*

An Infinite 200 Pro was used to determine the transparency of the silicone films. 6 mm discs were created using a biopsy punch for each film and placed in the solid sample holder before being continuously scanned at variable wavelengths (300 – 1000 nm per ISO 11979_2). Light source switches occurred at the 315 nm wavelength with a step size of 10 nm so as to not interfere with possible transition peaks. Data is reported as the percent of incident light transmitted through the films at each wavelength. For aqueous samples, the silicone discs were rinsed with DI water and the well plate used was filled with 100 μ L of DI water prior to testing.

2.5 **Statistical Analysis**

Reported values represent an average and standard deviation of triplicate measurements. Statistical analysis was performed using two factor ANOVA and statistical significance was defined with a p -value <0.05 .

3. RESULTS

3.1 Surface Chemistry

The hydrophilicity obtained from the water-driven surface restructuring of silicone films was analyzed by monitoring temporal changes in θ_{static} values. Generally, a $\theta_{\text{static}} > 90^\circ$ and $\theta_{\text{static}} < 90^\circ$ are considered to reflect hydrophobic and hydrophilic surfaces, respectively. A gradual, systematic decrease in the θ_{static} (i.e., from hydrophobic to hydrophilic) would be indicative of SMA PEO chains migrating to the surface upon contact of the modified silicone with water. Therefore, to monitor this process and to evaluate the ability of the modified films to retain SMA behavior post aqueous equilibration, θ_{static} were measured over a 2 min period after 2 weeks of both air and aqueous equilibration (Figure 3.1.A). During air equilibration, the unmodified silicone films, as expected, were very hydrophobic ($\theta_{\text{static}} > 110^\circ$) (Figure 3.1.A). Similarly, the silicone modified with the PEO-silane control (i.e., not amphiphilic) at 5 $\mu\text{mol/g}$ were hydrophobic but exhibited a modest decrease in θ_{static} for higher concentrations (i.e., 10 and 15 $\mu\text{mol/g}$). Interestingly the films modified with the PEO-silane control at 20 and 25 $\mu\text{mol/g}$ developed an appreciably hydrophilic surface. This effect was not observed in prior studies when the PEO-silane control was added at these higher concentrations to a “non-phenyl” containing silicone. At a given concentration of PEO-silane control, no modified silicone exhibited a marked decrease in θ_{static} during the 2 min period. Thus, for these modified silicones, the PEO-silane control does not appear to undergo water-driven restructuring. Rather, at higher concentrations, more of the additive localizes to the surface as the film forms. This behavior is most likely explained by the lack of a long siloxane tether, limiting the ability of the amphiphile to be mobile within the hydrophobic silicone matrix.

Our lab has previously demonstrated that siloxane tether length variations in PEO-silane amphiphiles are known to affect the efficacy of the restructuring process.¹⁰ Thus, two PEO-silane amphiphile SMAs having different tether lengths ($m = 13$ and $m = 30$) were evaluated. For silicones modified with the HDMS amphiphile with a tether length of 13 (*HDMS*, $m = 13$), at a concentration of 5 $\mu\text{mol/g}$, surfaces were similarly hydrophobic to that of the unmodified silicone and to the silicone modified. However, as the concentration of this amphiphile was increased, the surface restructuring became increasingly and appreciably significant. In particular, modified silicones prepared with higher concentrations of this SMA (20 and 25 $\mu\text{mol/g}$) were able to achieve an extremely hydrophilic surface at the end of the 2 min period (Figure 3.1.A). Their enhanced SMA behavior can be explained by the high compatibility of the siloxane tether with the silicone bulk, permitting superior migration of the PEO chains to the aqueous interface. For the PEO-silane amphiphile with the longer tether (*HDMS*, $m = 30$), modified silicones revealed an enhanced ability to undergo water-driven restructuring at a lower concentration of amphiphile (5 and 10 $\mu\text{mol/g}$). Higher concentrations of *HDMS*, $m = 30$ achieved maximum hydrophilic surfaces with lower θ_{static} values than silicone modified with *HDMS*, $m = 13$ (Figure 3.1.A). This distinctive ability of the *HDMS*, $m = 30$ amphiphiles to achieve very hydrophilic surfaces is thought to be attributed to the longer siloxane tether that further enhances solubility with the silicone matrix than *HDMS*, $m = 13$ and therefore facilitates migration of the hydrophilic chains of the amphiphile to the surface.

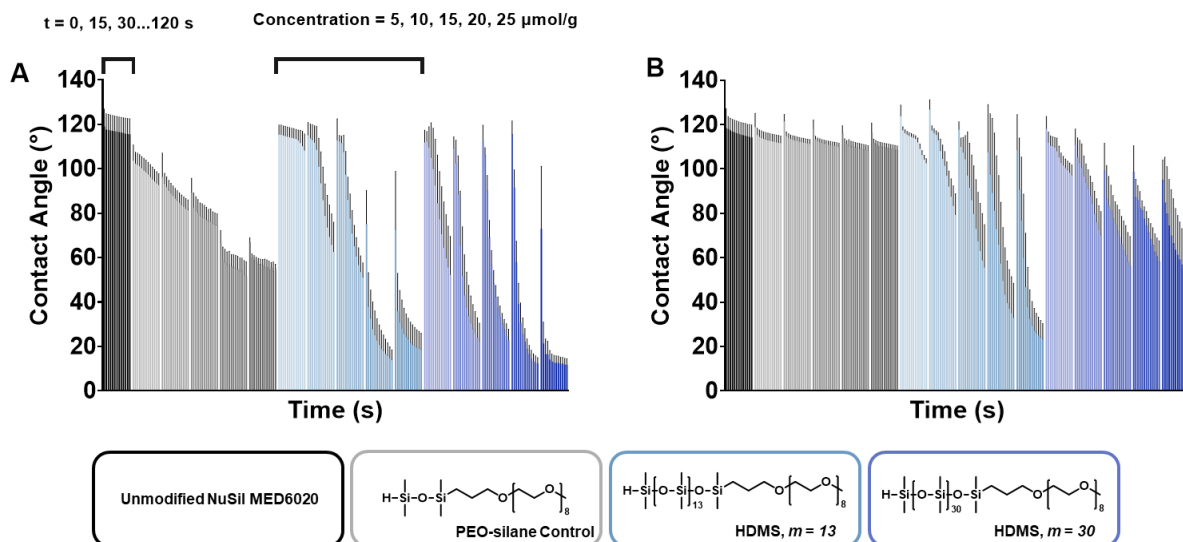


Figure 3.1. θ_{static} measured over a two min period in 15 sec intervals after two weeks of air equilibration (A) and after two weeks of aqueous equilibration (B). Groups of bars are arranged from left to right in order of increasing concentrations of SMA (5, 10, 15 and 25 μmol per 1 gram silicone.) Individual bars within a group represent increasing time points (0, 15, 30, 45, 60, 75, 90, 105, and 120 sec).

3.1.1 Aqueous equilibration

Surface wettability of the films was investigated after a two-week period of exposure to PBS at body temperature (37 °C) to assess the ability of the films to retain the surface reconstruction observed during the air equilibration. θ_{static} measurements revealed that the films modified with various concentrations of the PEO-silane control lost the ability to achieve a hydrophilic surface, even at high concentrations and after 2 min of water droplet deposition (Figure 3.1.B). Such behavior is thought to be due to the poor ability of the PEO-silane control as a SMA to migrate within the bulk silicone matrix due to the lack of a siloxane tether.

Unlike observations with the PEO-silane control, following aqueous equilibration, the silicones modified with *HDMS*, $m = 13$ retained their distinctive ability to undergo water-driven surface restructuring to achieve very low θ_{static} values. However, it can be observed that the final hydrophilicity of these films' surface is slightly lower than that of the equivalent set during the air equilibration (i.e., θ_{static} increased by $\sim 15^\circ$ or more). For silicones modified with the PEO-silane

amphiphile with the longer tether (*HDMS* $m = 30$), θ_{static} values following aqueous equilibration were significantly higher ($\sim 30^\circ$) than those seen in the air equilibrated set (Figure 3.1.B.). While this group of films had a limited ability to reach θ_{static} values $< 60^\circ$, some systematic decrease in θ_{static} during the 2 min was still apparent. We hypothesized that, for both SMAs, this behavior was due to the potential uptake of water into the films, reducing the thermodynamic potential of the PEO segments to migrate to the aqueous interface. It is speculated that more water was taken up by the silicones prepared with *HDMS*, $m = 30$, thereby reducing the potential for migration to the aqueous interface. The varying degrees of water uptake among modified silicones may be associated with the type of aggregate structures that form during cure.

3.2 Mechanical integrity

For a medical implant to have a safe and efficient performance inside the body, mechanical properties that closely match those of the native tissue are highly desired. Previously, R. F. Fisher determined that the modulus of elasticity of the lens capsule – the structure in the eye upon which an IOL is accommodated during cataract surgery – was around 1.5 MPa at 60 years of age.¹⁰ Additionally, the zonular fibers which are also important in the stability of the IOL position post-surgery have a Young's modulus of around 1.5 MPa.¹¹ Therefore, a material used for IOLs should desirably exhibit a modulus which is similar to that of the lens capsule and zonular attachments to perform safely after surgery.

Air equilibrated modified silicone films were subjected to tensile mechanical tests which revealed no statistically significant changes in modulus, stress at break, and strain at break (Figure 3.2.A.). These films exhibited a Young's modulus at 10% strain of around 1.0 MPa without significant variation from unmodified silicone films. Similarly, varying the siloxane tether length of *HDMS* amphiphiles resulted in no significant changes in both tensile stress and strain at break.

These results indicate that the extreme hydrophobicity of the silicone materials used for IOLs can be reduced using amphiphilic SMAs without compromising bulk mechanical properties – even at higher concentrations. Furthermore, the modulus of the silicone elastomer used in this study (with and without amphiphile) is relatively lower than that of the lens capsule and zonular fibers which should ideally allow for capsular bag deformation during cataract surgery to entrap the IOL and prevent its dislocation. Similarly, the tensile modulus falls within that of conventional elastomeric materials used for IOLs which have been demonstrated to be between 0.72 and 1.24 MPa.¹²

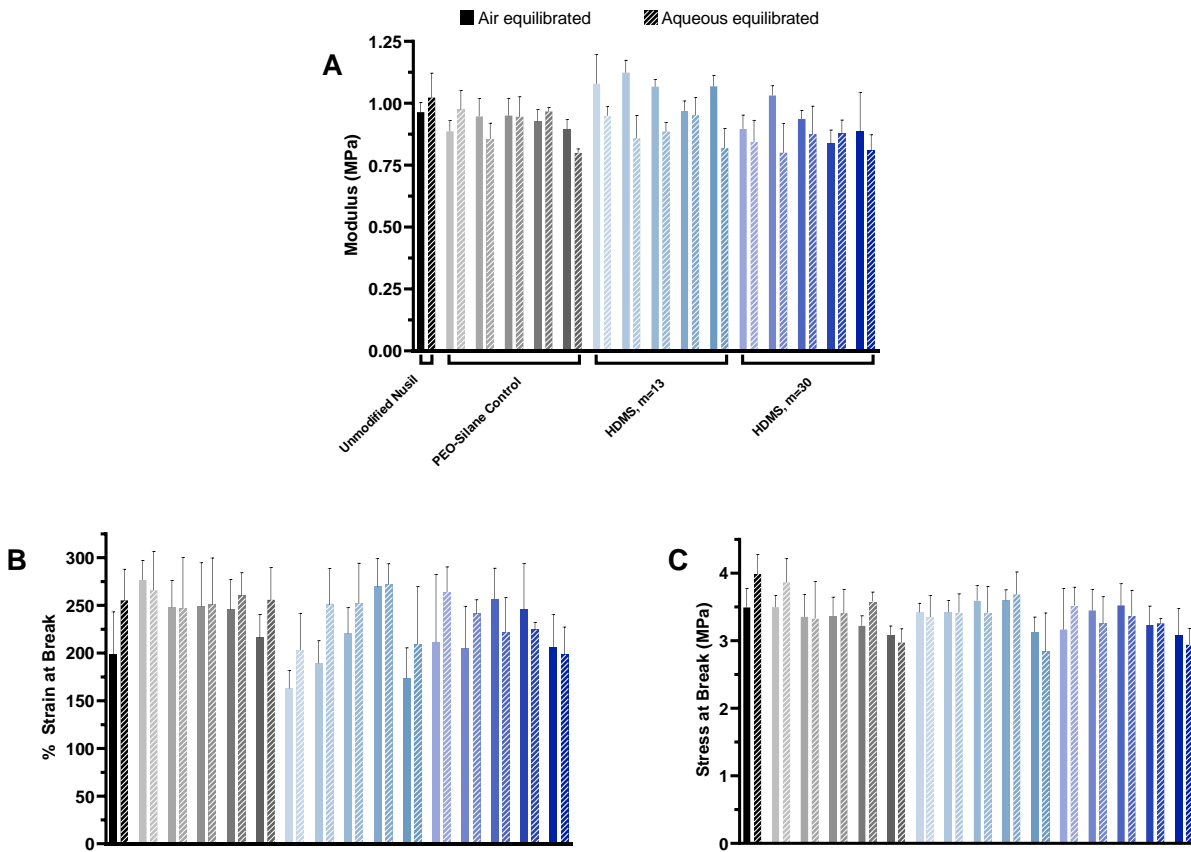


Figure 3.2. Tensile test results depicting modulus measured at 10% strain (A), % strain at break (B), and stress at break (C) for specimens following air- and aqueous equilibration.

3.2.1 *Aqueous equilibration*

Because an IOL is continuously subjected to the saline environment of the eye, it is important to evaluate the mechanical stability of materials intended for IOLs exposed to a physiologic environment. During this phase of the assessment, an equivalent set of silicone films were exposed to PBS at body temperature (37 °C) for two weeks. After the two-week period, the films were then subjected to the same mechanical test used for the films in air equilibration (Figure 3.2.B). Tensile tests revealed no significant change in modulus, percent strain, and stress at break after exposure to PBS at body temperature. The modulus of the aqueous equilibrated films at 10% strain was observed to be around 1.0 MPa for all films. Additionally, this value is still between the range that Christ et al. determined for conventional IOL elastomeric materials.¹² As expected, these results confirm that the surface modification achieved by incorporated SMAs do not compromise the bulk mechanical properties of the material – even after prolonged exposure to a physiologic environment.

3.3 **Optical Properties**

Equally important for the successful performance of a polymeric material in an IOL is the optical clarity of the material. Specifically, the silicone material used should be uniformly transparent. Therefore, a silicone modified with an SMA to form an IOL material should have the ability to achieve a more hydrophilic surface without compromising light transmittance. Following air equilibration, the transmittance test revealed that the unmodified silicone had ~85% transmittance (Figure 3.A). Additionally, all films modified with the amphiphilic SMAs resulted in light transmittance values slightly higher than the unmodified control except for the group of discs modified with the PEO-silane control at concentrations of 10 and 15 $\mu\text{mol/g}$. These films had slightly lower light transmittance values at ~80% (Figure 3.3.A). This behavior can be

explained by the aggregate hypothesis formulated earlier, where the short amphiphile chains with no siloxane tether tend to form small aggregates near the surface. After being exposed to PBS for two weeks at body temperature, this behavior was more apparent with higher concentrations of the PEO-silane control which lost transparency and fell to 70%, 74%, and 40% for concentrations of 15, 20, and 25 $\mu\text{mol/g}$ respectively (Figure 3.3.B). Meanwhile, the rest of the PEO-silane discs and those modified with *HDMS* $m = 13$, and $m = 30$ amphiphile had similar transmittance values to those of the unmodified control group at around 90%. Therefore, the incorporation of *HDMS* $m = 13$, and $m = 30$ amphiphiles as SMAs does not hinder the homogeneous transparency of the silicone material. Since most commercially available IOLs have light transmittance values above 89%, these amphiphilic SMAs hold strong potential to induce a hydrophilic surface without compromising the IOLs optical properties.^{12, 13}

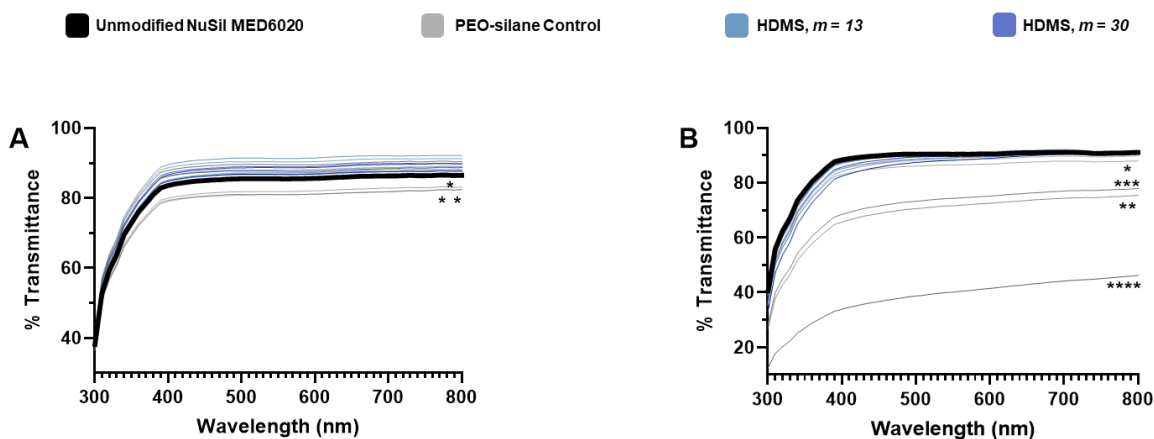


Figure 3.3. Light transmittance percent measured on 6 mm discs after air equilibration (A) and aqueous equilibration (B). PEO-silane 10 $\mu\text{mol/g}$ is represented with *, PEO-silane 15 $\mu\text{mol/g}$ with **, PEO-silane 20 $\mu\text{mol/g}$ with ***, and PEO-silane 25 $\mu\text{mol/g}$ with ****.

4. CONCLUSION

The present study has demonstrated that HDMS amphiphiles used as SMAs are effective at reducing the hydrophobicity of silicone materials intended for use in IOLs – even at low concentrations. When incorporated at concentrations of 20 and 25 $\mu\text{mol/g}$, the *HDMS, m=13* amphiphile can achieve distinctively high hydrophilic surfaces on silicone films (below 30° static contact angles). Moreover, the results demonstrate how the ability to undergo water-driven surface restructuring of silicone films modified with those concentrations of *HDMS, m = 13* is not impaired by prolonged exposure to PBS at physiological temperature. Aqueous equilibration of films modified with the *HDMS, m = 30* amphiphile, however showed decreased restructuring by $\sim 30^\circ$. Nonetheless, these films still showed a systematic decrease in contact angle which suggests that although an increasing tether length can initiate the formation of water aggregates, the increased steric interactions of the longer tether make them more uniformly dispersed. In the future, an AFM study of the amphiphile nanoscale features, as controlled by composition, would therefore more accurately provide insight into the interplay between amphiphile tether variations and the material surface.

Regarding the mechanical integrity of the modified silicones, incorporation of HDMS amphiphiles with tether lengths of 13 and 30 was shown to have no significant effect on modulus, strain at break, and stress at break. This result was observed on films in the air equilibration as well as those equilibrated in an aqueous solution. Additionally, silicone modifications with such HDMS amphiphiles as SMAs displayed no effect on the optical properties of the material in both air and aqueous equilibration. Light transmittance values remained at around 90% even after exposure to PBS.

Remarkably, these amphiphiles can strategically modify the surface of silicones and make them more hydrophilic without compromising both bulk optical and mechanical properties. The results obtained in this study are indicative of the superior potential and stability that HDMS amphiphiles have at reducing protein and subsequent LEC adhesion onto the surface of IOLs. The present study will be helpful in designing novel antifouling silicone materials that can be used to reduce PCO in IOLs.

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APPENDIX

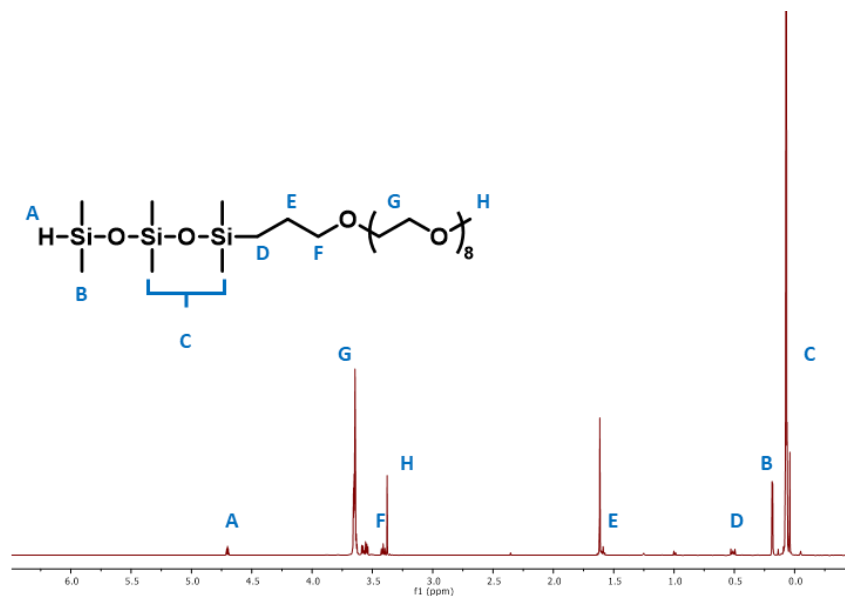


Figure A.1: ^1H NMR of “PEO-Silane”, (CDCl_3 ; δ , ppm): 0.05-0.10 (m, 12H, SiCH_3), 0.17-0.19 (d, $J = 2.8$ Hz, 6H, $\text{OSi}[\text{CH}_3]_2\text{H}$), 0.47-0.55 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.56-1.64 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 3.38 (s, 3H, OCH_3), 3.39-3.44 (t, $J = 6.9$ Hz, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 3.52-3.70 (m, 34H, $\text{CH}_2\text{CH}_2\text{O}$), 4.65-4.75 (m, 1H, SiH).

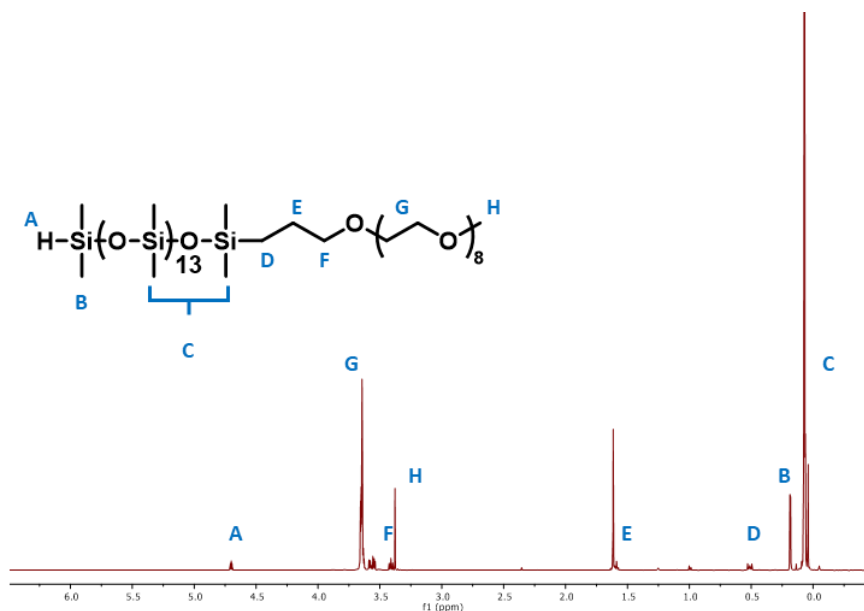


Figure A.2: ^1H NMR of “HDMS₁₃”, (CDCl_3 ; δ , ppm): 0.05-0.10 (m, 84H, SiCH_3), 0.17-0.19 (d, $J = 2.8$ Hz, 6H, $\text{OSi}[\text{CH}_3]_2\text{H}$), 0.47-0.55 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 1.56-1.64 (m, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 3.38 (s, 3H, OCH_3), 3.39-3.44 (t, $J = 6.9$ Hz, 2H, $\text{SiCH}_2\text{CH}_2\text{CH}_2$), 3.52-3.70 (m, 34H, $\text{CH}_2\text{CH}_2\text{O}$), 4.65-4.75 (m, 1H, SiH).

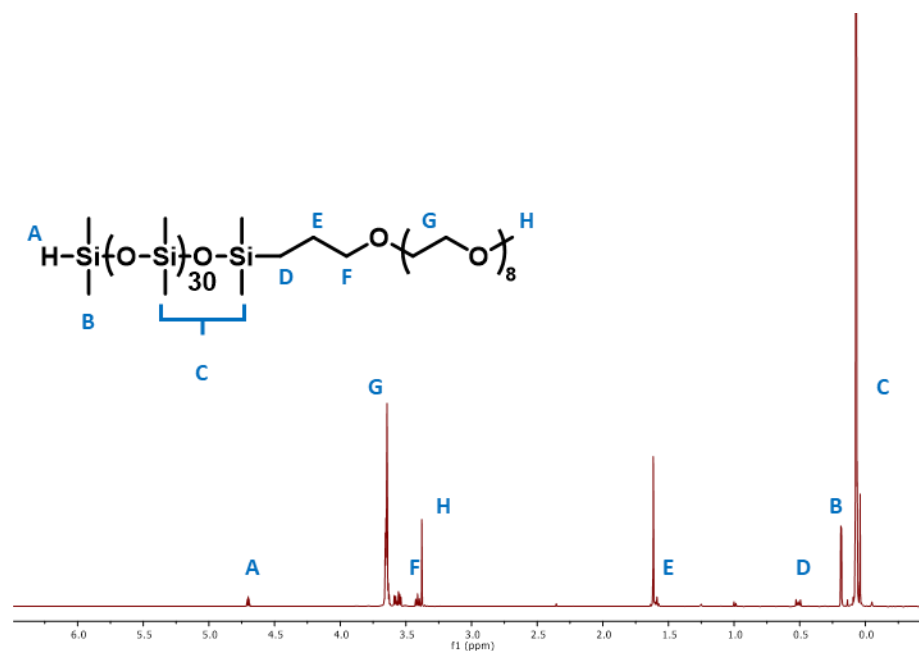


Figure A.3: ¹H NMR of “HDMS₃₀”, (CDCl₃; δ, ppm): 0.05-0.10 (m, 186H, SiCH₃), 0.17-0.19 (d, J = 2.8 Hz, 6H, OSi[CH₃]₂H), 0.47-0.55 (m, 2H, SiCH₂CH₂CH₂), 1.56-1.64 (m, 2H, SiCH₂CH₂CH₂), 3.38 (s, 3H, OCH₃), 3.39-3.44 (t, J = 6.9 Hz, 2H, SiCH₂CH₂CH₂), 3.52-3.70 (m, 34H, CH₂CH₂O), 4.65-4.75 (m, 1H, SiH).

Table A.1: Weight Percent Change Analysis

Film	Air Equilibration Weight (g)	Aqueous Equilibration Weight (g)	% Difference
Unmodified (μmol/g)			
0	0.4664	0.4663	-0.0178
TMDS (μmol/g)			
5	0.4785	0.4784	-0.0270
10	0.4602	0.4593	-0.1850
15	0.5023	0.5016	-0.1530
20	0.4797	0.4791	-0.1402
25	0.4711	0.4710	-0.0035
HDMS m=13 (μmol/g)			
5	0.4699	0.4697	-0.0360
10	0.4829	0.4824	-0.1040
15	0.4766	0.4760	-0.1271
20	0.4849	0.4847	-0.0245
25	0.4709	0.4704	-0.0918
HDMS m=30 (μmol/g)			
5	0.4688	0.4687	-0.0287
10	0.4678	0.4671	-0.1429
15	0.4700	0.4697	-0.0553
20	0.4749	0.4736	-0.2768
25	0.4677	0.4657	-0.4094