

Toward the Development of a Versatile Functionalized Silicone Coating

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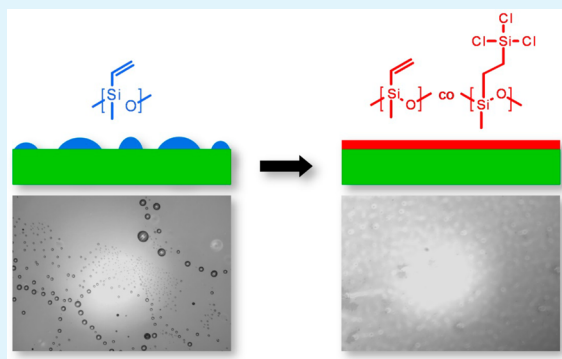
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S Supporting Information

ABSTRACT: The development of a versatile silicone copolymer coating prepared by the chemical coupling of trichlorosilane (TCS) to the vinyl groups of poly(vinylmethylsiloxane) (PVMS) is reported. The resultant PVMS-TCS copolymer can be deposited as a functional organic layer on a hydrophobic poly(dimethylsiloxane) substrate and its mechanical modulus can be regulated by varying the TCS coupling ratio. In this paper, several case studies demonstrating the versatile properties of these PVMS-TCS functional coatings on PDMS elastomer substrates are presented. Numerous experimental probes, including optical microscopy, Fourier-transform infrared spectroscopy, surface contact angle, ellipsometry, and nanoindentation, are utilized to interrogate the physical and chemical characteristics of these PVMS-TCS coatings.

KEYWORDS: silicone elastomer, trichlorosilane, poly(vinylmethylsiloxane), poly(dimethylsiloxane), thiol-ene, functional silicone



1. INTRODUCTION

Silicones, or polysiloxanes, are heterogeneous macromolecules composed of an inorganic Si–O backbone with alternating silicon and oxygen atoms and two pendant organic groups attached to each silicon atom.^{1,2} They are employed in a wide variety of contemporary applications ranging from electronics and personal care to automotive, biomedical and construction technologies.^{3–7} Poly(dimethylsiloxane) (PDMS), the most common silicone employed in a broad range of technologies, possesses a very low glass transition temperature ($T_g \approx 150$ K) primarily due to considerable backbone flexibility. In addition, the presence of two stable methyl groups attached to the silicon atom endows PDMS with exemplary chemical and physical resistance. For instance, because of attractive/repulsive interactions, these groups become oriented parallel to the surface at an air interface, but prefer to stay buried under the polymer backbone at a water interface, to adopt their lowest energy configuration. In contrast, because of fixed bond angles arising from steric hindrance, pendant methyl groups attached to hydrocarbon backbones are more rigid and thus much less environmentally responsive.⁸

Because of their low T_g values, silicones exist as liquids at ambient temperature. When they are chemically cross-linked, however, they form flexible silicone elastomers (SEs) with an elastic modulus of ~ 1 MPa, but individual chains remain liquid-like between cross-link junctions. The high flexibility of the Si–O backbone ensures that SEs continue to adopt the lowest energy conformations while responding to changes in the environment. Because of their commercial availability, low cost,

and chemical inertness, SEs have been applied in diverse biomedical technologies, including contact lenses and human implants, which require that the surface of PDMS be hydrophilic to minimize factors such as corneal discomfort and platelet adhesion, respectively.⁹ Increasing the surface energy of intrinsically hydrophobic PDMS¹⁰ can be achieved by chemical modification, physical alteration,^{11–16} a combination of both chemical^{17–25} and physical treatment,^{26–28} or simple physisorption.^{29–32} In spite of these efforts, achieving stable PDMS-modified surfaces remains a challenging task.³³ Because chemical oxidation of SEs tends to rely on strong acids or bases that either render variable results or compromise network integrity, the surfaces of SEs are more controllably modified by physical means involving plasma, corona, and ultraviolet/ozone (UVO) processes, as well as high-energy electron and ion beam exposure.^{34–36}

Although plasmas employ one or more ionized gases (often including oxygen) to introduce hydrophilic surface groups on the surface of PDMS by converting the pendant methyl groups to polar moieties, it likewise generates a brittle, relatively thick silica-like layer because of irreparable degradation to the polymer backbone caused by de/repolymerization.^{37–41} Mismatch between the mechanical properties of this rigid layer and flexible PDMS results in the formation of surface cracks that gradually permit silicone oligomers to diffuse to the surface and

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consequently reduce the hydrophilicity (generally referred to as hydrophobic recovery).^{42–46} Oxygen plasma can be replaced by UVO treatment, described in detail elsewhere,^{47–53} to produce similarly hydrophilic species in a thin PDMS surface layer. Compared to plasma modification, UVO surface treatment can yield chemically similar changes under significantly milder, but slower, conditions. The nearly order of magnitude increase in exposure time required^{47–53} allows for improved control over surface conversion, because different degrees of hydrophilicity can be obtained at different treatment times. Extended UVO treatment times (≥ 60 min) can nonetheless generate a thin silica-like surface layer (~ 5 nm thick) with a density that is 50% of that of pure silica.⁴⁸ Mechanical deformation of this bilayered laminate can result in the formation of wrinkles/buckles.^{54–57}

Replacing a methyl group on PDMS with a vinyl group yields poly(vinylmethylsiloxane) (PVMS), which is much more chemically tailorable than PDMS.⁵⁸ While the properties of PVMS are generally similar to those of PDMS,⁴⁹ the added vinyl groups afford access to alternative chemical modification pathways. For instance, Efimenko et al. have demonstrated that the UVO treatment time needed to make the surface of PVMS hydrophilic is considerably shorter (ranging from seconds to a few minutes) than that of PDMS due to the higher susceptibility of vinyl groups.^{59,60} The presence of vinyl groups on PVMS also permits straightforward chemical modification. In the present work, we couple trichlorosilane (TCS) to PVMS via hydrosilylation to form random copolymers consisting of unmodified (VMS) and modified (VMS-TCS) units. Upon exposure to moisture, the chlorosilane groups convert quickly and quantitatively into silanol (Si–OH) groups, which enable facile attachment to various substrates while concurrently cross-linking the PVMS-TCS networks through condensation among the Si–OH groups. We note that other modification strategies of PVMS are possible, such as a thiol–ene reaction with functional thiols. As described in subsequent sections, we use the latter class of reactions to deliver specific functionality to PVMS-TCS coatings by having them react with specific thiol-based modifiers.

Here, we exploit both functions concurrently to cross-link and attach thin PVMS-TCS coatings to solid surfaces during spin-coating, thereby further modifying their surface properties. This strategy offers unique opportunities for tailoring the physical and chemical characteristics of functional silicone coatings. The chemical composition of the copolymer (as well as its network density, modulus and surface adhesion) can be tuned by varying the concentration of TCS, which allows further modification of unreacted vinyl groups by, for example, thiol–ene coupling to achieve protein/scratch-resistant and self-cleaning coatings.

2. EXPERIMENTAL SECTION

Materials. Poly(vinylmethylsiloxane) was synthesized using step-growth polymerization of short hydroxyl-terminated oligomeric vinyl methyl siloxane chains, as reported previously.^{49,58,59} Briefly, the precursor monomer was obtained by slow hydrolysis of methylvinyl-dichlorosilane in the presence of dilute aqueous HCl solution. The reaction products comprised various vinylmethyl siloxane cycles (VD3, VD4 and VDS) and linear hydroxyl-terminated chains. The cyclic products were separated by vacuum distillation to obtain linear chains with a yield of ~ 25 – 35% , depending on the quantity of HCl and water present in the reaction mixture. All polymers used in the experiments were prepared from hydroxy-terminated linear chains. Solvent-free siloxane polymerization was initiated by a small amount of lithium hydroxide (10–20 ppm) at 100 °C for various reaction times under

constant nitrogen flow that facilitated the removal of water molecules formed during the reaction. The reaction was terminated by the addition of carbon dioxide, which resulted in the formation of α,ω -hydroxy terminated PVMS chains. The final polymer was vacuum-filtered using the Celite 545 filtering aid system. Unreacted short oligomeric chains were removed by precipitation in methanol. The resulting PVMS was first dissolved in diethyl ether and then added dropwise to chilled methanol. Polymer was collected and dried under a vacuum for 72 h. This procedure was repeated two times. Size-exclusion chromatography equipped with light scattering and refractive index detectors verified the complete removal of low-molecular-weight compounds, yielding monomer conversions very close to 92%. Infrared spectroscopy confirmed that the amount of vinyl functional groups remained unchanged, which suggested that no backbone branching occurred, during the polymerization. The experiments described in this study were conducted using only hydroxy-terminated PVMS with a molecular weight of 35 kDa.

1H,1H,2H,2H-Perfluorinated decanethiol (F8H2-SH) was purchased from Oakwood Chemical Products Inc. (West Columbia, SC) and used as-received, whereas ω -thiol terminated poly(ethylene glycol) methyl ether (PEG-SH, 5 kDa) was purchased from Polymer Source Inc. (Quebec, Canada). Trichlorosilane, as well as reagent-grade anhydrous toluene, anhydrous tetrahydrofuran (THF), chloroform, acetone, methanol, and ethanol, were all purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification. In addition, α - ω -vinyl-terminated PDMS (62 kDa), tetrakis-(dimethylsiloxy)silane (TDSS), and Pt(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex were obtained from Gelest Inc. (Morrisville, PA).

Chemical Functionalization. The hydrosilylation reaction involved in coupling TCS to PVMS was performed in the presence of the Pt(0) complex in anhydrous toluene (or THF). Liquid PVMS was dissolved in toluene at predetermined concentrations in a glass vial, and an amount of TCS needed to achieve a selected conversion was then added to each PVMS solution (**Caution: TCS reacts violently with water and liberates HCl. Refer to the MSDS sheet of TCS for safety guidelines**). The Pt(0) complex was added to every vial, which was subsequently capped under nitrogen. The reaction mixture was stirred with a magnetic stir bar for ~ 1 – 2 h at ambient temperature. For instance, the PVMS-TCS solution with a concentration of 3.0% (w/w) and a vinyl:TCS ratio of 7.0 was prepared by mixing 0.6 g of PVMS (6.98 mmol vinyl groups) and 100 μ L of TCS (0.99 mmol) in 20 g of dry toluene. The physical properties of the coating are tabulated as a function of vinyl:TCS ratio and PVMS-TCS solution concentration in Figure S1 in the Supporting Information.

Additional chemical modification of PVMS was conducted to functionalize the PVMS-TCS coatings. Before the incorporation of TCS, a fraction of the pendant vinyl groups on PVMS was modified in solution via a thiol–ene addition reaction involving two different thiol molecules (F8H2-SH and PEG-SH), which were first reacted with PVMS in dry THF in quartz vessels under light ($\lambda = 254$ nm) for 12 h at ambient temperature. A portion of the remaining vinyl groups was then coupled with TCS in the presence of the Pt(0) catalyst under the conditions listed above to introduce cross-linkable groups. We routinely used the PVMS-TCS solutions to prepare coatings immediately after TCS coupling, with the results reported herein always being reproducible. We have also tested the stability of the PVMS-TCS solutions. In particular, we stored the PVMS-TCS solutions in glass vials with PTFE lined caps to prevent exposure to moisture, which would otherwise promote cross-linking. A vast majority of the vials filled with coating solution remained in liquid form for many months.

Film Preparation. Films of cross-linked PDMS and PVMS with thicknesses measuring ≈ 600 μ m were prepared by mixing the polysiloxane base, cross-linker, and catalyst in predetermined amounts, followed by vigorous stirring and degassing under reduced pressure to remove trapped air bubbles. The mixtures were then cast into Petri dishes and cured at ambient temperature for 24 h and then at 70 °C for 72 h (**Caution: These experiments should be performed in a fume hood because gaseous HCl is produced when PVMS-TCS is exposed to**

moisture at ambient conditions). For direct coating functionalization, PVMS-TCS solutions in toluene were spin-coated onto PDMS by using a Headway Research PWM-32 instrument at a speed and acceleration of 2000 and 1000 rpm/s, respectively, for 60 s (the same safety rules indicated above should be followed). Concentrations of solutions used for spin-coating PVMS-TCS layers on PDMS supports or silicon wafer ranged from 0.5 to 5.0% w/w. The quantity of HCl liberated upon exposing the TCS groups to ambient moisture is low and does not compromise the stability of the siloxane networks.⁶¹

Ultraviolet/Ozone (UVO) Treatment. The UVO treatment of selected materials was conducted in a commercial UVO chamber manufactured by Jelight Company, Inc. (Model 42). The source used was a standard fused quartz lamp that emits about 65% of its total radiation at 184.9 nm and has an output of 6.2 mW/cm² at a distance 6 mm away from the source, as measured by a UV light detector. Substrates of interest were placed on glass slides and inserted into the UVO chamber at a distance of ~10 mm from the lamp to promote surface modification for predetermined periods of time.

Coating Characterization. Water contact-angle (WCA) experiments were performed via the sessile drop technique with deionized water (resistivity >15 MΩ-cm) using a Ramé-Hart Model 100–00 contact-angle goniometer equipped with a CCD camera. Data were analyzed with the Ramé-Hart Imaging 2001 software. The WCAs were determined after placing an 8 μL droplet of deionized water on each surface of interest. At least 4 different measurements were performed across the sample surface, and average WCA values are reported along with their corresponding standard errors. The thicknesses of films deposited on nontransparent substrates were measured by variable-angle spectroscopic ellipsometry (VASE) on a J.A. Woollam Co. instrument. All ellipsometric data were collected at an incidence angle of 70° with respect to the surface normal and at wavelengths ranging from 400 to 1100 nm in 10 nm increments. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet 6700 spectrometer, and the data were analyzed by means of the Omnic software. Transmission FTIR was used to monitor the extent of coupling reaction, whereas FTIR performed in attenuated total reflection (ATR) was employed to follow chemical changes that occurred on coatings after surface modification. In the first case, a drop of PVMS-TCS solution extracted at the end of the coupling reaction was spread on a KBr crystal, and spectra were collected after complete solvent evaporation. Spectra of surface-modified films were collected in ATR mode with a Ge crystal. For each sample, 256 scans were collected and averaged (after correcting for the background) at a resolution of 4 cm⁻¹. The mechanical properties of PVMS-TCS coatings on PDMS substrates and silicon wafers were tested with a Hysitron Triboindenter operated in quasi-static mode and equipped with an integrated atomic force microscope.⁶² Indentations were performed at ambient temperature with a 46 μm conical diamond tip after calibration on standard fused quartz. Force–displacement curves of the indents were analyzed by the Oliver-Pharr method with the TriboScan software. According to this procedure, the reduced modulus (E_r) is first calculated from $(S/2)/(\pi/A)^{1/2}$, where S represents the initial stiffness (slope) of the unloading curve and A is the projected contact area. The Young's modulus of the measured sample (E_s) is subsequently obtained from

$$E_s = (1 - \nu_s^2) \left[\frac{1}{E_r} - \frac{(1 - \nu_i^2)}{E_i} \right]^{-1} \quad (1)$$

where ν denotes Poisson's ratio, with assigned values of $\nu_s \approx 0.5$ for SE and $\nu_i = 0.06$ for the indenter. For a standard diamond indenter probe, the modulus (E_i) is 1140 GPa.

Gas permeation measurements were performed on an in-house constructed constant-volume/variable-pressure cell.⁶³ Specimens of measured thickness (l) were sandwiched between aluminum tape with openings of known area (A), permitting O₂ to permeate through the polymer membrane. After applying moderate vacuum (~200 mTorr) to both sides of the membrane, O₂ was introduced at a known pressure on the upstream side of the membrane. The downstream pressure was recorded upon gas permeation through the SE membrane. Using the

known downstream volume (V), the permeability (P) of O₂ can be calculated from

$$P = \frac{Vl}{ART\Delta p} \frac{dp}{dt} \quad (2)$$

where R is the universal gas constant, T denotes absolute temperature, Δp corresponds to the difference between upstream and downstream pressures, and dp/dt refers to the steady rate of pressure increase on the downstream side. The permeability of O₂ was calculated under the conditions of an upstream pressure of 2 atm at 23 °C.

3. RESULTS AND DISCUSSION

To render the hydrophobic PDMS surface hydrophilic, one can employ a plethora of modification methods discussed earlier. Hydrophilization of PDMS surfaces by chemical means requires the use of relatively harsh chemical treatments that may alter the network structure close to the substrate. Preparation of hydrophilic PDMS surfaces without compromised mechanical and permeation properties through the use of physical means, e.g., plasma or UVO treatment, likewise remains an ongoing challenge. Here, we first endeavor to avoid PDMS hydrophilization altogether by fabricating surface-functionalized PVMS/PDMS bilayered laminates, as schematically illustrated in Figure 1. In one protocol aimed at yielding PVMS/PDMS

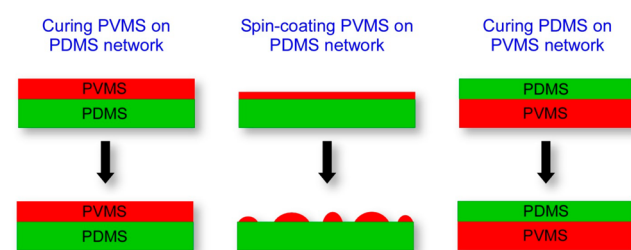


Figure 1. Possible routes by which to form bilayers of silicone elastomers (SEs) composed of PVMS and PDMS.

sandwich layers, a macroscopic PVMS coating is applied to a PDMS substrate and cured in-place. This approach, however, yields a poor PVMS elastomer because of deleterious migration of low-molecular-weight cross-linking agents across the polymer/polymer interface from the PVMS layer into the PDMS substrate. The same problem arises in the converse arrangement, that is, if liquid PDMS is coated onto a cross-linked PVMS substrate (cf. Figure 1). To reduce the amount of PVMS cross-linker needed, we have spin-coated a thin layer of PVMS on top of a PDMS substrate, but this produces an unstable coating that undergoes dewetting as consequences of both thermodynamic incompatibility and autophobicity between PVMS and PDMS. The latter effect has been confirmed by spin-coating PDMS liquids with various molecular weights onto cross-linked PDMS and observing that they all dewet. For these reasons, we have elected to couple a cross-linkable moiety to PVMS to stabilize PVMS coatings and prevent their dewetting from cross-linked PDMS surfaces.

The functional group chosen here is TCS (depicted in the PVMS-TCS copolymer in Figure 2), which, in the presence of moisture, immediately hydrolyzes to Si–OH groups that can cross-link. The chemical composition of each PVMS-TCS copolymer is discerned from the number of vinyl groups coupled with TCS. The extent of coupling can be tuned by changing the vinyl:TCS ratio in the reaction medium and measured by monitoring the area under the vinyl peaks

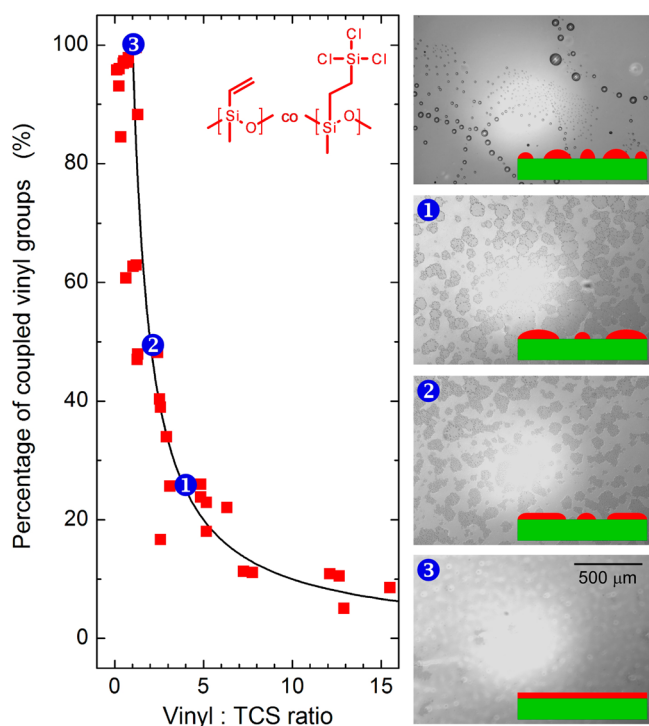


Figure 2. (Left panel) Percentage of reacted vinyl groups in PVMS with TCS as a function of the vinyl:TCS ratio. The inset depicts the chemical structure of a PVMS-TCS random copolymer. (Right panel) Optical images ($5\times$ magnification) and graphical illustrations of PVMS-TCS coatings (red) on PDMS substrates (green). Except for the case of pure PVMS (top), the number labels next to each optical micrograph correspond to PVMS-TCS samples with vinyl:TCS ratio >0 ; those are marked on the plot in the left panel.

corresponding to known PVMS vibrations in FTIR spectra: C=C twist/ $=\text{CH}_2$ wagging ($\sim 960\text{ cm}^{-1}$), $=\text{CH}_2$ scissor ($\sim 1407\text{ cm}^{-1}$), and C=C stretch ($\sim 1587\text{ cm}^{-1}$). Figure 2 displays the percentage of reacted vinyl groups measured as a function of the vinyl:TCS ratio, along with theoretical values (black line) calculated on the basis of complete vinyl:TCS coupling. The favorable agreement between experimental measurements and theoretical values apparent in Figure 2

provides strong evidence for the quantitative nature of the vinyl:TCS reaction. Spin-coating the PVMS-TCS copolymer coatings onto PDMS elastomer substrates clearly reveals that the stability of the coating increases by increasing the extent of vinyl:TCS coupling. Optical micrographs of such spin-coated layers, as well as corresponding graphical illustrations, are included in Figure 2. In each case, the thickness of the spin-coated PVMS-TCS layer remains below $\sim 50\text{ nm}$, as measured by ellipsometry of identical films deposited onto silicon wafer.

Whereas pure PVMS completely dewets from (and exhibits islands on) cross-linked PDMS, the coatings composed of PVMS-TCS with 25% and 50% TCS display discrete holes that are indicative of improved stability. In addition, the sizes of the holes decrease with increased TCS coupling. When all the vinyl groups in PVMS are reacted, the spin-coated layers become completely defect-free and stable. In light of these observations, we propose that a stable PVMS-TCS copolymer layer forms when the rate of cross-linking exceeds the rate of dewetting during spin-coating. Cross-linking (even partial) of PVMS-TCS serves to stabilize the surface layer by decreasing chain mobility, which in turn reduces the tendency of films to dewet from the PDMS support. An alternative route to enhance the stability of PVMS surface coatings relies on increasing the coating thickness. In general, PVMS-TCS coatings on PDMS substrates become increasingly more stable when the thickness of the spin-coated layers is increased beyond $\sim 50\text{ nm}$. Such film stability allows investigation of contiguous PVMS-TCS coatings at intermediate degrees (less than 100%) of reacted vinyl groups. The thickness of PVMS-TCS films (as measured on silicon wafer) is presented as functions of the vinyl:TCS ratio and concentration of PVMS-TCS copolymer in the spin-coating solution in Figure 3a. As intuitively expected, the film thickness increases significantly as the PVMS-TCS copolymer concentration is increased. Increasing the extent of TCS coupling also yields marginally thicker films because of the larger number of available cross-linkable TCS groups, but this effect is much less pronounced.

An increase in the number of cross-linkable TCS groups in the PVMS-TCS copolymer translates into an increase in the density of cross-links, which effectively densifies the network by decreasing the molecular weight between cross-link sites. This effect also serves to improve the stability of the PVMS-TCS

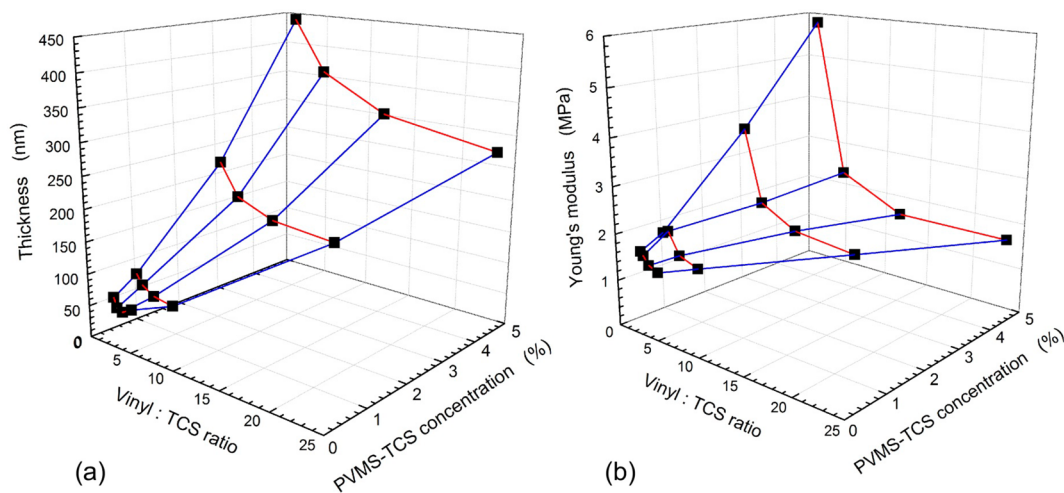


Figure 3. (a) Thickness and (b) Young's modulus of PVMS-TCS coatings as functions of PVMS-TCS solution concentration and vinyl:TCS ratio. The lines serve to connect the data. The raw data used to generate these plots are provided in the Supporting Information.

surface coating (cf. Figure 2) and is expected to affect the stiffness (Young's modulus) of the PVMS-TCS coating. Modulus values extracted from nanoindentation measurements are provided in terms of the vinyl:TCS ratio and PVMS-TCS copolymer concentration in Figure 3b and demonstrate that film thickness (correlated with the spin-coating solution concentration) does not strongly influence the mechanical properties of the surface layer except at low vinyl:TCS ratios (near complete vinyl:TCS coupling). Because the thickness of these PVMS-TCS coatings is less than the penetration depth of the indenter tip, however, these modulus values represent a composite modulus of the coating and PDMS substrate, which explains why the invariant modulus values match the modulus of the PDMS elastomer (~ 1.4 MPa for 62 kDa PDMS). Another probe of cross-link density and film thickness is gas permeation. Although a thin PVMS-TCS film with a low cross-link density would be anticipated to exhibit a high permeability, increases in film thickness or cross-link density would have the opposite effect. The data shown in Figure 4 reveal that SEs

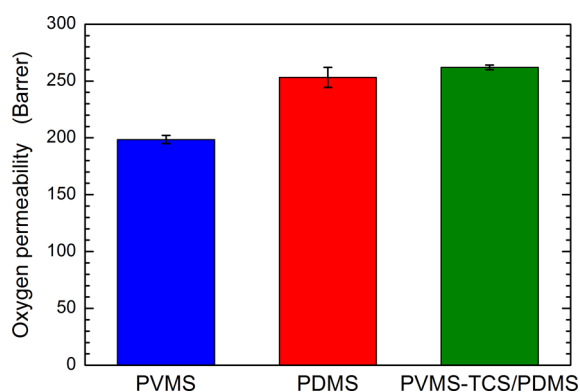


Figure 4. Oxygen permeability through SEs composed of PVMS, PDMS and PVMS-TCS-coated PDMS. In the latter case, the thickness and vinyl:TCS ratio of the PVMS-TCS coating are ~ 150 nm and 7, respectively. The values reported represent the average of 3 measurements; the error bars correspond to the standard error.

derived from PVMS and PDMS possess measurably different oxygen permeabilities. Addition of a PVMS-TCS surface coating measuring ~ 150 nm thick (with a moderate vinyl:TCS ratio = 7) on a PDMS support has no discernible effect, which establishes that these coatings can be designed at the molecular level to have little impact on the mechanical and transport properties of PDMS elastomer substrates.

The wettability and chemical composition of PVMS-TCS/PDMS laminates have been interrogated by WCA and FTIR measurements, respectively, at varying vinyl:TCS ratios and copolymer concentrations (i.e., film thicknesses) before and after UVO treatment for 10 min (chosen on the basis of WCA data identifying when UVO-treated PDMS and PVMS elastomers first become hydrophilic with WCA values less than 90°). Figure 5a shows WCA results for bare (untreated) SE; $106.3 \pm 2.3^\circ$ for PDMS and $96.7 \pm 2.7^\circ$ for PVMS; and four series of PVMS-TCS/PDMS laminates. In the case of the laminates, the WCA generally decreases from the level of bare PDMS to the level of bare PVMS, and the surface becomes correspondingly more wettable, at vinyl:TCS ratios less than 10 and solution concentrations greater than 0.5%, but the PVMS-TCS surface nonetheless remains hydrophobic. Coatings deposited from solutions at a concentration of 0.5% display evidence of high WCA values primarily because they dewet

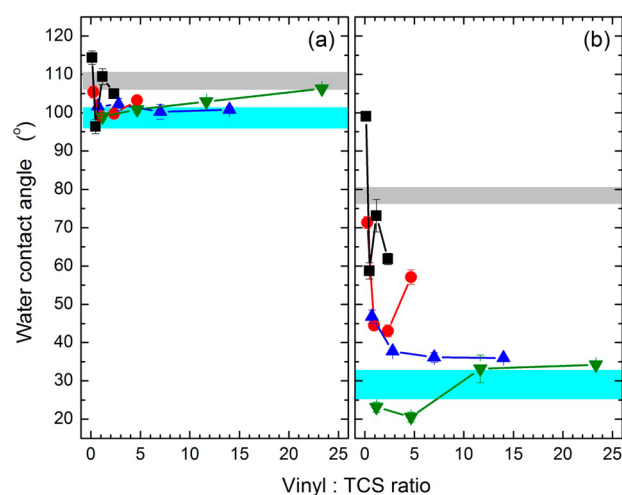


Figure 5. Water contact-angle (WCA) data of PVMS-TCS coatings on PDMS substrates as a function of the vinyl:TCS ratio (a) before and (b) after 10 min of UVO treatment for four different PVMS-TCS solution concentrations (in %): 0.5 (black square), 1.0 (red circles), 3.0 (blue up-triangle), and 5.0 (green down-triangle). The gray and light blue regions in a and b signify the WCA range for bare PDMS and PVMS elastomers, respectively.

from, and consequently roughen, the surface of the PDMS substrate. After UVO treatment, however, the WCA values of the bare elastomers drop substantially to $76.4 \pm 2.2^\circ$ for PDMS and $29.1 \pm 3.8^\circ$ for PVMS, thereby verifying that the surfaces have become hydrophilic in Figure 5b. Although the UVO-treated PVMS-TCS/PDMS laminates generally show a considerable reduction in WCA from that of bare PDMS, PVMS-TCS coatings deposited from solutions at a concentration greater than 1% exhibit WCA values that are comparable to that of bare PVMS.

The FTIR-ATR spectra corresponding to the PVMS-TCS/PDMS laminates discussed in relation to Figure 5 are presented in Figure 6a for the case of no UVO treatment and Figure 6b for UVO treatment (10 min). In Figure 6a, an increase in the PVMS-TCS layer thickness on the PDMS substrate results in an increase in the intensity of the vinyl peaks located at 960, 1407, and 1600 cm^{-1} , with the spectra gradually resembling that of bare PVMS. This transition is expected since the probing depth of FTIR-ATR (performed on a Ge crystal) is $\sim 1\ \mu\text{m}$, and an increase in PVMS-TCS thickness is accompanied by an increase in the PVMS-TCS signal. Analogous FTIR-ATR spectra acquired after UVO treatment are displayed in Figure 6b and indicate that new peaks appear because of the presence of hydroxyl (3300 and 940 cm^{-1}) and carboxyl (1725 cm^{-1}) groups.^{59,49} The intensity of these peaks increases with increasing coating thickness, and the spectrum collected from the PVMS-TCS layer spin-coated from 5% copolymer solution appears identical to that of the bare PVMS elastomer. Therefore, we conclude from Figures 5 and 6 that the wettability and chemical composition of the PVMS-TCS/PDMS coating after UVO treatment for 10 min closely resembles that of UVO-modified PVMS.

Because of their inherent biocompatibility and high gas permeability, SEs have been employed in a wide range of biomedical devices, including contact lenses. For this particular application, both surfaces of each lens must be rendered hydrophilic to (1) facilitate permeation of oxygen and water vapor through the elastomer, (2) improve lubrication between

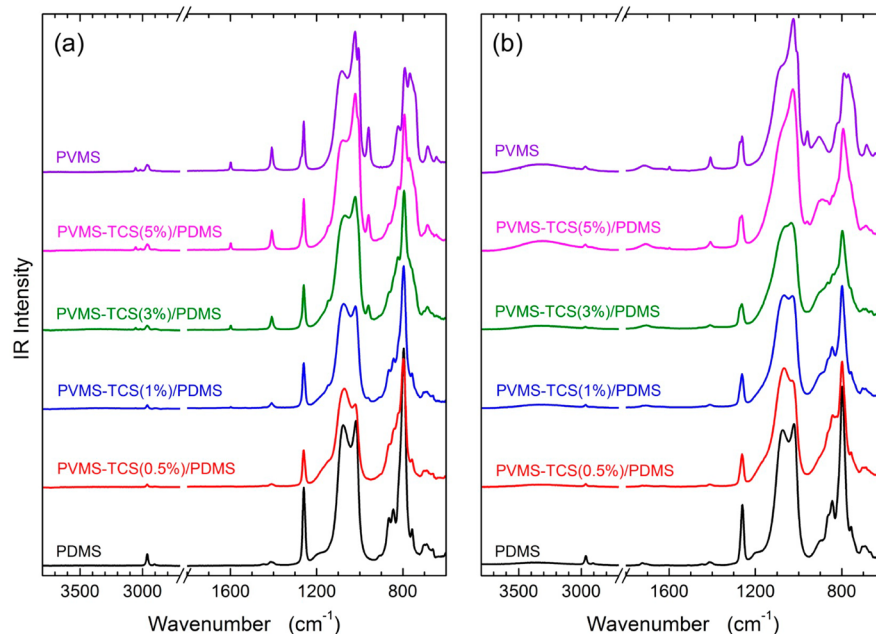


Figure 6. FTIR-ATR spectra acquired from SEs and SE laminates (a) before and (b) after 10 min of UVO treatment. Included here are color-coded/labeled spectra for bare PDMS, PVMS-TCS/PDMS laminates with PVMS-TCS coatings prepared at four different solution concentrations (%): 0.5, 1.0, 3.0, and 5.0, and bare PVMS.

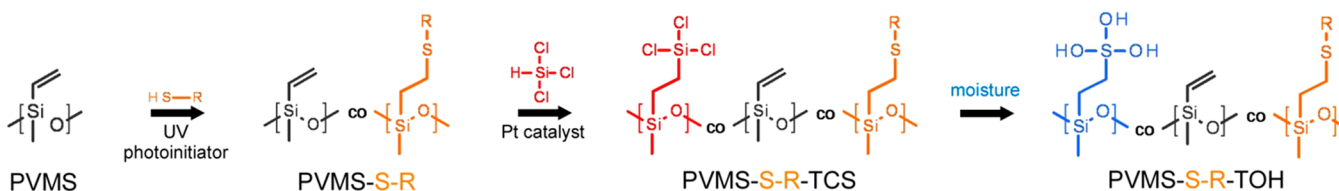


Figure 7. Reaction scheme depicting the chemical insertion of a thiol into the PVMS-TCS coating to promote added functionality.

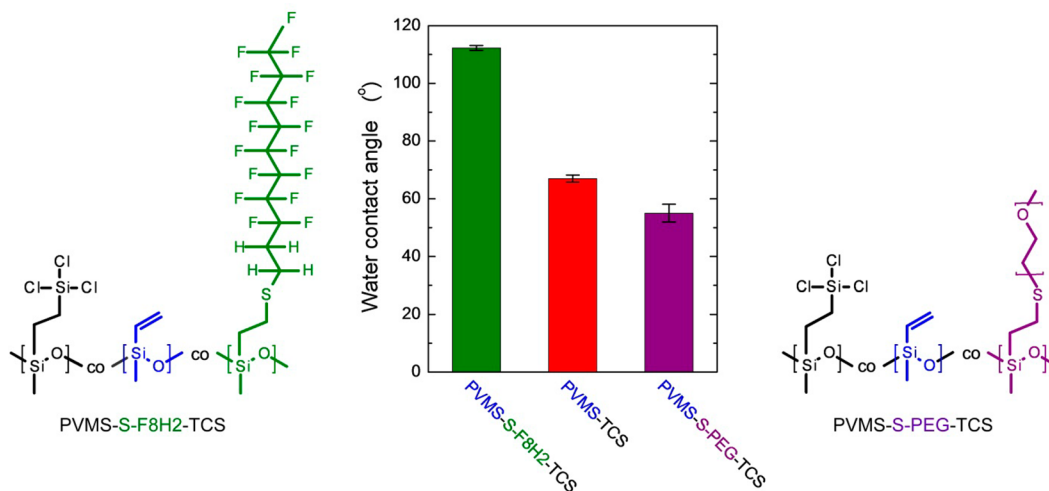


Figure 8. Chemical structures of fluoroalkane (left) and PEG (right) functional coatings derived from PVMS-TCS and their corresponding wettabilities measured by static WCA. The values reported represent the average of 3 measurements, and the error bars correspond to the standard error.

the lens and eyelid, and (3) minimize biofouling such as protein adsorption from tear fluid. Surface modification of contact lenses is currently accomplished by grafting protein-repellent groups, such as poly(ethylene glycol) (PEG), to the surfaces of PDMS-based contact lenses by first exposing the lenses to cold oxygen plasma, which activates the surfaces, and then

chemisorbing PEG chains. Although this approach yields hydrophilic protein-repellent surfaces, lens durability is compromised because the surface coating is relatively thin and, as such, eventually suffers from hydrophobic recovery, as well as mechanical failure. On the basis of the results reported in Figure 5, increasing the hydrophilic layer thickness would be

an obvious route by which to improve the lifetime of lenses, but doing so is not straightforward. With this intention in mind, the functionality of PVMS-TCS coatings deposited on PDMS surfaces has been examined here as a viable alternative by exposing the remaining vinyl groups in PVMS-TCS coatings to a thiol-ene addition reaction intended to introduce protein- and scratch-resistant moieties into the coatings.^{64–67}

Details of the thiol-ene reaction are provided in the Experimental Section, and the general reaction scheme is displayed for completeness in Figure 7. For illustrative purposes in this study, we have elected to incorporate two distinctively different thiols into our PVMS-TCS coatings, a thiol-terminated fluoroalkane (F8H2-SH) and a thiol-terminated PEG (PEG-SH), to generate hydrophobic and hydrophilic surfaces, respectively, in controllable fashion. The chemical structures of the resultant functional copolymers are presented in Figure 8. Included here are WCA values measured from coatings of these copolymers spin-coated from 1% solutions onto silicon wafer. As anticipated, attachment of fluorinated groups to the coating render the surface hydrophobic with a WCA of $112.3 \pm 0.8^\circ$, which is slightly more than the WCA of untreated bare PDMS (cf. Figure 5a). In marked contrast, inclusion of the PEG oligomers yields a hydrophilic surface with a WCA of $55.1 \pm 3.1^\circ$, which is lower than that of the unfunctionalized PVMS surface and, thus, even more hydrophilic. Unlike the layer of grafted chains discussed earlier with regard to surface hydrophilization of contact lenses, the PVMS-TCS-thiol copolymers produced in this study constitute contiguous SEs that are expected to be more mechanically robust and resilient than grafted chains alone. The chemical changes accompanying thiol functionalization of the PVMS-TCS coatings have been monitored and confirmed by FTIR-ATR (data not shown).

4. CONCLUSIONS

Emerging applications incessantly drive the need to develop new types of surface coatings or surface-modification processes that result in the expeditious fabrication of functional materials deposited on flexible and transparent substrates. Flexible electronics, including the manufacture of displays, novel platforms for sensory detection, and more reliable contact lenses, are just a few contemporary examples. Many of these applications employ relatively inert polymeric substrates that are not readily modified via traditional chemical approaches. Although the modification of such surfaces by physical means is possible, the methods commonly employed involve plasma or coronal treatments that promote surface degradation, which may ultimately compromise the desired mechanical, optical, or electrical characteristics of the substrate. Strategies are therefore continually required for identifying alternative modification routes that would involve less harsh and more versatile means of controllably altering the surface properties of flexible polymeric supports.

In this work, we report on the development of thin cross-linkable functional copolymer coatings generated by (1) coupling trichlorosilane (TCS) with the vinyl groups of PVMS in the presence of a Pt(0) catalyst at ambient temperature and (2) subsequently spin-coating the resulting PVMS-TCS copolymers directly onto PDMS substrates. The silane coupling is tunable, quantitative and controlled by the vinyl:TCS ratio in the reaction mixture. The thickness and modulus of the coating can be altered by varying the vinyl:TCS ratio and the concentration of the copolymer in the spin-

coating solution. The stability and quality of PVMS-TCS coatings on PDMS substrates improves with increasing PVMS:TCS coupling due to faster “immobilization” of PVMS-TCS chains that cross-link on the PDMS surface. Postdeposition UVO treatment of PVMS-TCS coatings on PDMS substrates greatly promotes surface wettability, with WCA values of the coatings approaching those of UVO-treated PVMS. In addition, we have established that PVMS-TCS coatings can be further chemically functionalized via thiol-ene addition to introduce hydrophobic or hydrophilic moieties for more precise surface control. In a forthcoming publication, we demonstrate the ability of PVMS-TCS to coat other polymeric supports and discuss potential applications of such coatings.

■ ASSOCIATED CONTENT

Supporting Information

Additional figure and table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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