

When Ultimate Adhesive Mechanism Meets Ultimate Anti-Fouling Surfaces—Polydopamine Versus SLIPS: Which One Prevails?

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What happens when the extremely adhesive and versatile chemistry of polydopamine (PDA) is in contact with the extremely slippery surfaces known as slippery liquid-infused porous substrates (SLIPS)? Inspired by the pitcher plant, SLIPS possess excellent repellence against a variety of complex liquids and have been proposed as promising antifouling surfaces because of their successful performance even in marine environments. In the counterpart, inspired by the adhesive proteins enabling the strong adhesion of mussels to multiple substrates, PDA has been extensively studied for its ability to adhere on nearly every type of substrate. The interaction between various SLIPS systems and the highly fouling medium from the oxidative polymerization of dopamine is explored here. A PDA coating is observed on all the SLIPS evaluated, modifying their hydrophobicity in most cases. In-depth study of silicone-based SLIPS shows that hydrophobicity of PDA coated SLIPS partially recovers with time due to percolation of the lubricant through the coating. “Strongly” bound PDA species are attributed to the formation of dopamine-polydimethylsiloxane species on the crosslinked matrix, rendering a coating that withstands repeated washing steps in various solvents including water, hexane, and toluene. The results not only satisfy scientific curiosity but also imply a strategy to modify/bond SLIPS.

1. Introduction

Stickiness and slipperiness are opposite properties both with very important roles in the fields of surface chemistry, material

science, and biology. Considerable attention has been paid to the natural strategies in seeking to reproduce the key aspects that make the natural world so efficient in achieving these tasks.^[1] In the matter of stickiness, mussels are brought into the spotlight. Their extraordinary adhesion to diverse substrates even under wet conditions is mainly attributed to the 3,4-dihydroxy-L-phenylalanine (DOPA) and lysine-enriched proteins. These proteins are predominant in the byssus they secrete to attach to a surface.^[2] These findings have inspired the application of dopamine as a universal coating and linking material since 2007.^[3] Dopamine is a molecule with both the catechol structure of DOPA and the amine group of lysine. The derivatives from the oxidative polymerization of dopamine, generally referred to as polydopamine (PDA), can easily deposit on nearly all types of substrates, including perfluorinated and superhydrophobic surfaces. The exact polymerization mechanism, adhesion mechanism and structure


of PDA remain elusive. However, it is generally accepted that both covalent and non-covalent interactions are involved in the polymerization and binding of PDA to substrates.^[3d,4] This adhesive versatility is attributed to the presence of the nucleophilic and electrophilic reactive sites in its structure.

On the opposite extreme, the ultra-slipperiness observed on the wet slide of carnivorous plants,^[1b] has inspired the development of surfaces with almost perfect slipperiness against various materials and against a genetically diverse range of organisms.^[5] SLIPS, first developed by Aizenberg et al.,^[5a] are created by infusing porous membranes or textured substrates with liquid lubricants. The lubricant is stabilized on the surface as mid-term structural component retaining its liquid-like mobility.^[6] The properties of SLIPS do not rely on the formation of air pockets and they can tolerate high pressure conditions; this makes them very promising marine anti-fouling coatings. Their functionality has been demonstrated for small marine species, including spores and cypris^[5b] and also against larger organisms such as seashells.^[7] In the latter case the extreme effective softness provided by the lubricant layer, fools the specialized probing mechanism of mussels which searches for a solid counterface to adhere.

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Very recently, the competition between SLIPS and PDA has raised scientific curiosity. In a self-lubricant slippery gel made from silicone, resistance of universally adhesive PDA was observed.^[8] However, such resistance not always occurs. In this study, we have evaluated the performance of various SLIPS systems and the silicone-based SLIPS more in-depth against PDA coating solutions and found that under certain conditions PDA can actually form a stable coating on SLIPS surfaces. We also seek to provide further understanding of the coating mechanism of PDA on SLIPS. Our results on one hand provide bases to improve the performance of SLIPS against this type of fouling but on the other hand imply a possible method to modify SLIPS or bond SLIPS on substrates.

2. Results

2.1. PDA Coating of Various Types of SLIPS

We first verified the deposition of PDA on various SLIPS systems, including infused membranes and swelled polymeric matrices where a “nanoporous” structure is provided by crosslinked polymer networks. For this, fluorinated- and silicone-based lubricants (F-oil and Si-oil, respectively) were used to infuse polypropylene (PP) and polytetrafluoroethylene (PTFE) membranes and to swell a crosslinked fluoropolymer and a silicone. These four kinds of SLIPS systems are widely used for various anti-fouling coatings and thus selected for demonstration.^[5a,b,e,7,9] These specimens were separately immersed in freshly prepared dopamine solution 2 mg mL^{-1} in phosphate buffer with a pH adjusted to 8.5 with NaOH. The specimens remained in this oxidative polymerization solution for 24 h under constant stirring (see Experiment Section). As observed in **Figure 1**, a PDA coating was formed on each of these slippery substrates. Color PDA coatings were observed on all

substrates indicating the failure of the anti-fouling property of these SLIPS. In most cases the initial hydrophobic behavior was changed to hydrophilic with the PDA coating, with the only exception of the system formed by F-oil-infused PTFE membrane (PTFE + F-oil) which retained a rather similar hydrophobic behavior despite the PDA coating.

It has been suggested that the thickness of the lubricant layer on these slippery systems is crucial to maintain the anti-fouling properties of the substrates,^[9] and therefore, the swelled systems offer an improved endurance in the long run due to a continuous release of lubricant. Under this consideration and due to the higher environmental affinity of silicones, we selected the silicone-based swelled system to further study the interaction between PDA and SLIPS.

2.2. Oil Replenishment of Silicone-Based SLIPS

Polydimethylsiloxane (PDMS) elastomers with a thickness of $\approx 1 \text{ mm}$ were swelled in Si-oil (10 cSt) to produce the SLIPS used in this study. After complete swelling of the specimens (Figure S1, Supporting Information), the excessive oil was removed from the surface by dabbing, that is, gently pressing a lint-free tissue against the surface. The viscosity of 10 cSt for the lubricant in these SLIPS was chosen as a compromise between durability and functionality. The viscosity of the lubricant plays a very important role in the antifouling functionality of SLIPS. While a high viscosity lubricant provides a better stability because it is more difficult to wash it off from the surface by rolling drops or by a flow, a lubricant with low viscosity ensures a high mobility of the species landing on the surface and thus enabling a faster shedding-off from them (Figure S2, Supporting Information); overall reducing or preventing the contact with the solid substrate. To ensure consistency throughout our experiments, the thickness of the

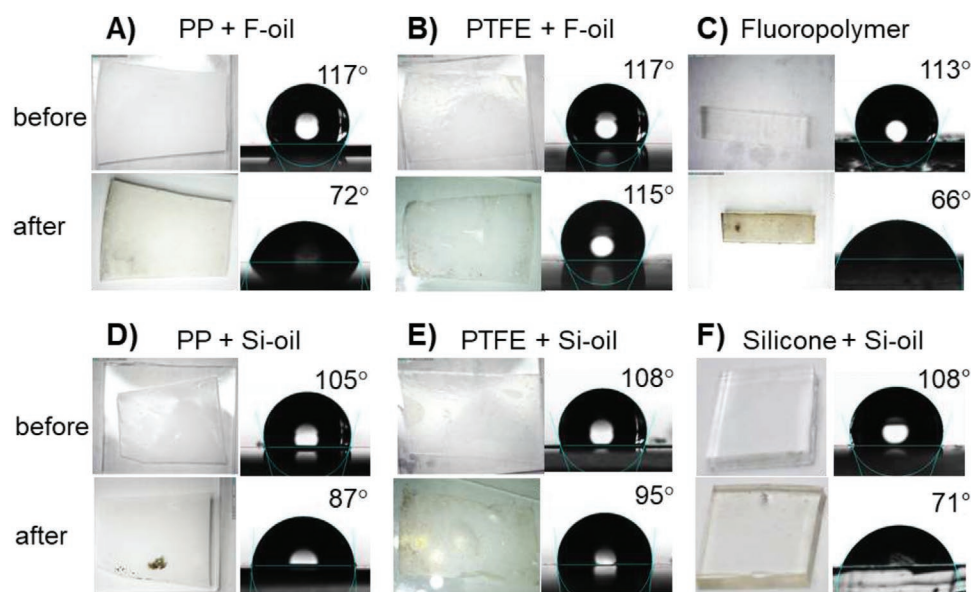


Figure 1. Various SLIPS systems before and after 24 h exposure to PDA. A) PP membrane with F-oil, B) PTFE membrane with F-oil, C) fluoropolymer infused with F-oil, D) PP membrane with Si-oil, E) PTFE membrane with Si-oil, and F) PDMS swelled in Si-oil. Reduced contact angle in all cases with the exception of B).

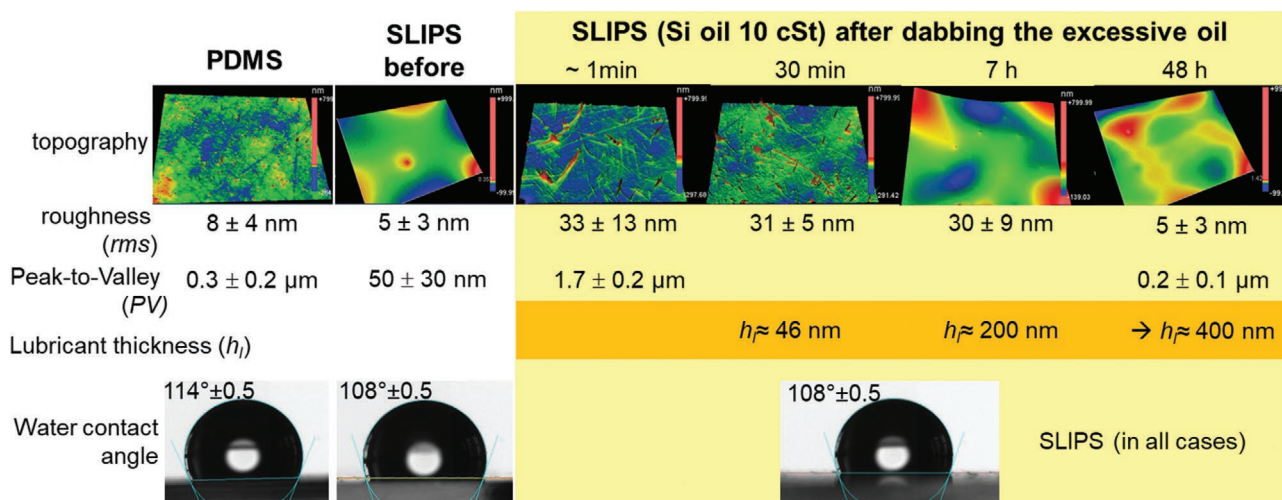


Figure 2. Initial PDMS surface and evolution of a SLIPS surface after dabbing of the lubricant.

lubricant layer (h_l) was monitored until reaching a relatively stable thickness on the fully swelled PDMS and the time required to achieve it. This was done by a combined analysis with refractometry and ellipsometry (Figures S3 and S4; Tables S1 and S2, Supporting Information). **Figure 2** shows, from left to right, the initial PDMS surface before swelling, the surface of the fully swelled PDMS drained by gravity and before removal of the excessive oil by dabbing, and the gradual evolution of the SLIPS surface after dabbing. The originally smooth surface of PDMS (root-mean-squared, $rms \approx 8$ nm) becomes rougher in the SLIPS ($rms \approx 33$ nm) after dabbing the top layer of oil. However, as the oil inside the swelled matrix creeps out to recover the SLIPS, it renders a “smoothing” effect on the surface lowering its rms and peak-to-valley (PV) values and progressively reaching a stable thickness of ≈ 400 nm after about 48 h. Noteworthy is that the specimens remain slippery despite the removal of excess of lubricant from the surface, which means that there is a ubiquitous lubricant layer throughout our experiments. The contact angle remains similar in all SLIPS surfaces at about 108° which is slightly smaller than that for PDMS of 114° . The fast replenishment of lubricated surfaces observed here is similar with the previous results.^[9] Such replenishment was supposed to enhance the anti-biofouling performance of SLIPS but could not prevent the formation of PDA coatings.

2.3. PDA Coatings

We monitored the formation of PDA coating on SLIPS substrates by collecting samples immersed in the polymerizing solution of dopamine for different times. **Figure 3** shows the topography, the images, and the water contact angle (WCA) of these samples; the topography images share the same scale in z (-3000 to $+3000$ nm). Two different coating scenarios are shown in this figure: still and stirred. Two sets of SLIPS were evaluated under each coating scenario, one set of specimens had a time-stable lubricant layer ($h_l \approx 400$ nm) and the other set had their top oil layer freshly dabbed ($h_l \approx 36$ nm). Scanning electron microscopy (SEM) images of the same

specimens are shown in Figure S5, Supporting Information. In these images the deposition of PDA species on the SLIPS is observed already after 1 h of exposure to the polymerizing solution. With longer exposures, the PDA coating becomes more homogeneous and covers a larger extension of the surface. The clear visualization of the PDA coating is achieved after 6 h of immersion when the coating becomes sufficiently thick to render a yellow coloration to the SLIPS. In contrast, the samples immersed in a control buffer solution (pH: 8.5) without PDA display the same appearance and WCA after immersion (Figure S6, Supporting Information). The PDA species adhere to the SLIPS surface with enough strength to overcome the multiple washing steps. These consisted of pipetting fresh water or dipping the coated specimen in clean water and gently shaking it while immersed (Video S1 and S2, Supporting Information). A similar outcome was observed in SLIPS with Si-oil of higher viscosity exposed to the polymerizing solution for 24 h, these results are included in Figure S7, Supporting Information. It is noted that the species loosely bound or entrapped in the outermost layer of the surface, that is, on the lubricant layer, can be easily removed by washing treatment.^[8] However, in the case of PDA species strongly bound to the solid substrate, they remain on the surface even after washing treatment with solvents that remove the oil from the surface, including hexane and toluene. Delamination appeared favored only after successive washings with solvents that rapidly and greatly swell PDMS such as chloroform; the cyclic expansion and contraction of the PDMS produced by the fast swelling and de-swelling of PDMS partially peeled-off the coating from surfaces (Figure S8, Supporting Information). Acetone and isopropanol did not affect the coating. This indicated that the PDA species were not only floating on the lubricant layer but they actually engaged in contact with the crosslinked PDMS matrix. The coating was robust enough to withstand repeated dipping in water and rinsing with different solvents, but the mechanical removal of the PDA coating was possible by scratching or pressing with a certain load (Section 10, Supporting Information).

From the roughness analysis, it can be observed that the constant stirring of the reacting solution renders rougher

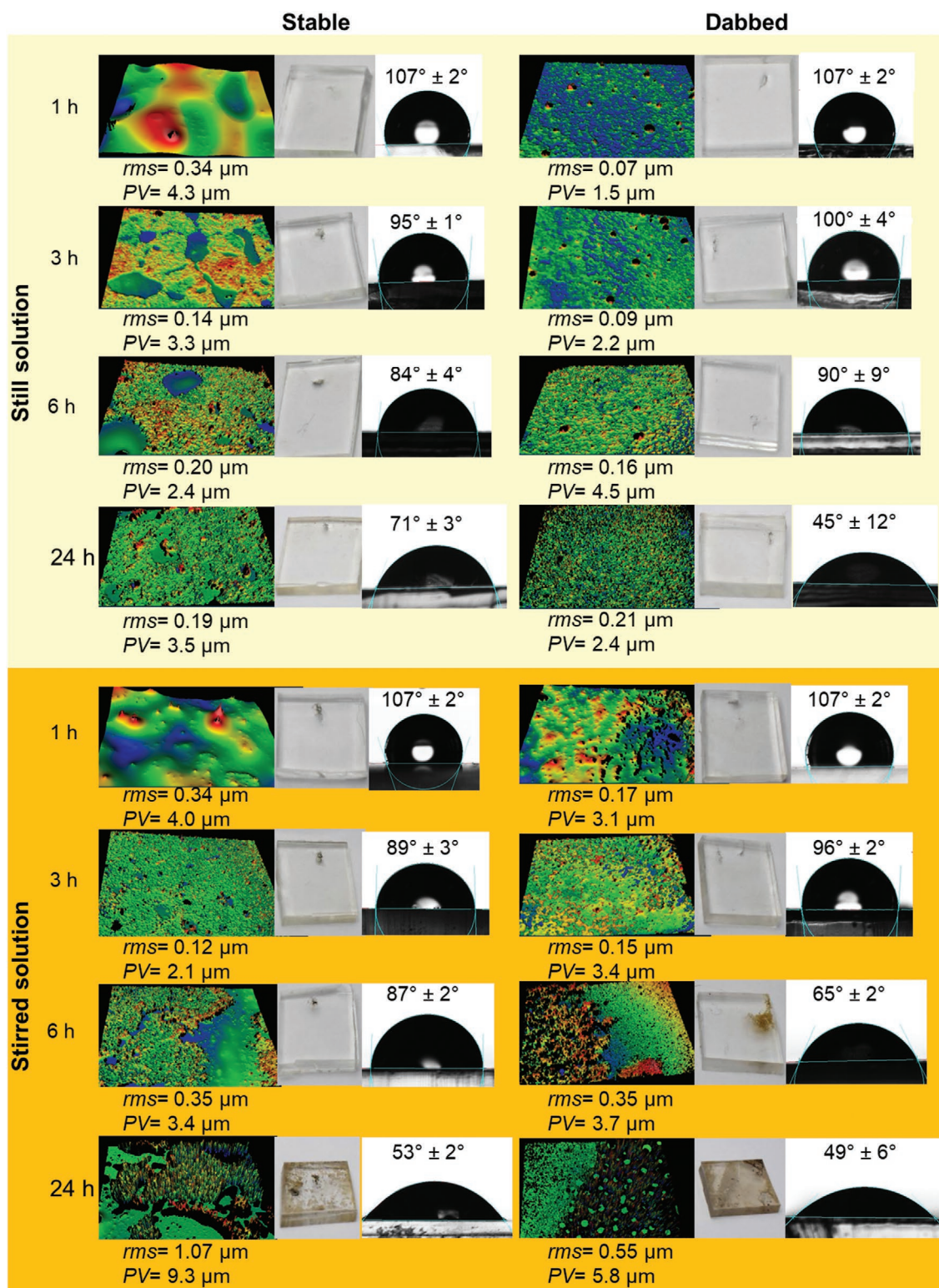


Figure 3. PDA coatings at increasing time on silicone-based SLIPS at two deposition conditions: still and stirred. Series labeled as stable refer to SLIPS with lubricant layer of thickness about 400 nm and series labeled as dabbed refer to specimens with lubricant layer recently wiped resulting in a thickness of ≈ 36 nm.

PDA coatings. We attributed this to the improved circulation of larger PDA aggregates, resulting from an also faster polymerization process or from delamination of sufficiently thick

PDA film, and thus improving their probability to adhere or re-adhere to the surface. From the comparison between images of both sets of SLIPS, the PDA coating is more uniform on

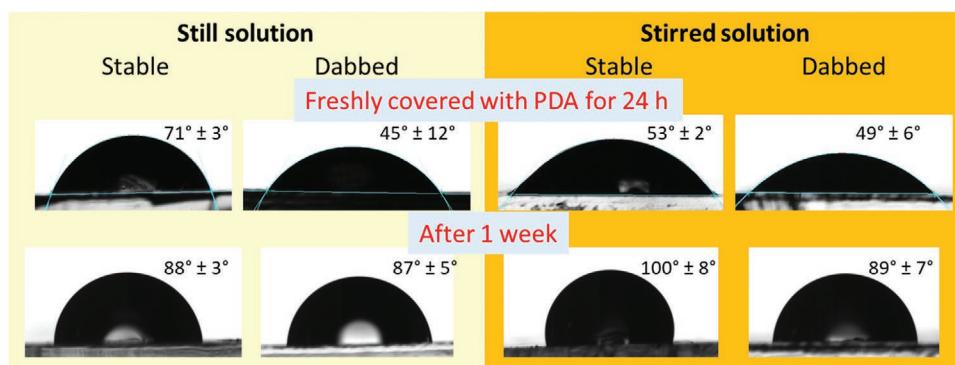


Figure 4. Contact angle recovery with time because of the lubricant percolation through the PDA coating to re-cover the surface.

the SLIPS with thinner lubricant layer. The thicker lubricant layer seemed to provide longer protection against the extremely fouling PDA species, but at the same time appeared to act as a potential trap for the larger PDA aggregates. This is observed in the larger particles deposited on the SLIPS with stable lubricant layer. After reaching a certain thickness, the coating is prone to delamination which is clearly observed in the images after 6 h of coating under stirring (also in Figure S5, Supporting Information). The coatings obtained under still conditions appeared smoother and thinner according to the interferometric, SEM, and visual inspection. These results clearly demonstrated that the PDA coating was imminent for these lubricant thicknesses in both stirred and still conditions.

2.3.1. Hydrophobicity Change

Further evidence of the PDA coating on the SLIPS was obtained from the wettability change after exposure to the PDA solution. The WCA measurements in Figure 3 were done within 15 min after removal of the SLIPS from the PDA solution, after washing with water and drying. The default nature of the silicon-based SLIPS is hydrophobic; with WCA of $\approx 108^\circ$. No significant changes were observed within the 1 h of exposure to PDA. The increase in exposure time of SLIPS to the PDA solutions reduces its WCA sequentially. This is an indication of a gradually improved coverage of the slippery hydrophobic surface by the hydrophilic PDA species. Specimens exposed to the PDA solution for a period longer than 6 h came out completely wetted and showed hydrophilic behavior in subsequent washing steps. In general, a lower WCA was observed from coatings on the specimens with thinner lubricant layer labeled as “dabbed.” This agrees with the previous observation that for a similar exposure time, a more uniform or thicker PDA coating is deposited on SLIPS with a thinner lubricant layer, thus showing better wettability. The higher roughness rendered by a continuous stirring of the PDA solution improved the wettability of the surface in all cases; this is observed in the lower WCA of the coatings from a stirred solution in comparison to those with the same exposure time from a still solution.

The low contact angles observed in the freshly prepared PDA coatings on SLIPS did not remain constant. With time, the surfaces partially recovered their hydrophobic behavior due to the

percolation of the Si-oil from the swelled PDMS matrix through the PDA coating. This resulted in a PDA coating somewhat covered with lubricant. **Figure 4** shows the change in WCA of the SLIPS coated for 24 h as freshly prepared (last row Figure 3) and after 1 week. Although the original WCA of SLIPS is not fully recovered, a large increase in the contact angle is evident. The “cloaking” phenomenon, or accumulation of lubricant at the edge of water drops on these PDA coated SLIPS, exhibited a similar behavior to that observed in clean SLIPS (Figure S9, Supporting Information), which leads to oil shedding from the surface.

In a supplementary experiment with a dopamine polymerizing solution containing similar concentration of dopamine 2 mg mL^{-1} and pH 8.5 adjusted with NaOH, but with ten times lower concentration of phosphate buffer (PBS 1 mM and NaCl 0.0154 M), no PDA coating was observed on the SLIPS after 12 h of immersion (Figure S10, Supporting Information), and no obvious change in their wettability. The dopamine polymerization reaction, however, resulted on the typical dark colored solution. This shows that not only the pH, nor the initial concentration of dopamine alone, is important for the coating of these SLIPS. It is the combined role of salts concentration, together with dopamine and NaOH that contribute to the complex coating mechanism.

2.3.2. Chemical Composition of the Coatings

To validate the presence of the PDA coatings on the SLIPS specimens, the elemental composition of the coatings was studied by energy-dispersive X-ray spectroscopy (EDX). **Figure 5** shows the SEM image and the corresponding EDX spectrum of a SLIPS with a stable layer of lubricant after 24 h exposure to a stirred PDA solution. Only the four elements C, N, O, and Si are present in the residual coating after the multiple washing steps. The presence of dopamine species can be confirmed with the presence of the peak around 0.4 keV corresponding to the $K\alpha$ emission of nitrogen.

2.4. Fouling Ability of an Aged PDA Solution

Formation of PDA coating on substrates is a complicated process involving various active species formed during the

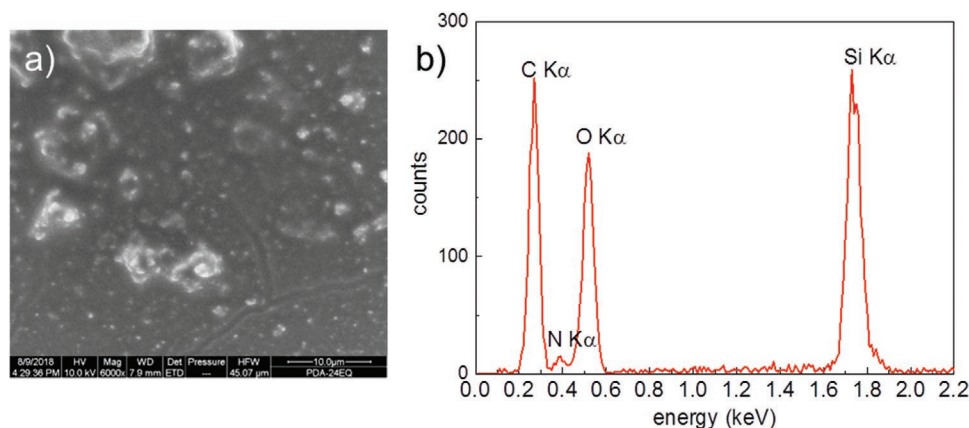


Figure 5. Elemental analysis by EDX of the PDA coating after 24 h under stirred condition on a SLIPS with equilibrium layer of lubricant (≈ 400 nm). a) Scanned area and b) EDX spectrum with 10 keV.

immersion of substrates in the dopamine polymerization solution. To gain further insight into the adhesive mechanism of PDA on SLIPS, we evaluated the ability of the PDA solution to coat the SLIPS specimens at different stages from the beginning of the polymerization reaction, that is, at increasing aging time. For this, different specimens were introduced in a PDA solution after determined aging time and remained immersed in the reacting solution for 24 h. The resulting coatings are shown in **Figure 6**. From these results, it appears that regardless of the stage of the polymerization, a PDA coating deposits on the SLIPS when it remains immersed in the solution for at least 24 h. Within the first 48 h of polymerization herein evaluated, the dopamine derivatives in the solution retain their extreme fouling ability. These observations challenge previous findings suggesting that the most critical species for the PDA coating deposition are formed in the early stages of the polymerization reaction of dopamine.^[4b,10] On the other hand, these observations support to certain extent the claims from Hong et al.^[4a] and Dreyer et al.^[11] suggesting the

existence of un-polymerized dopamine units trapped within the structure of PDA, which could in time provide the linkage with the crosslinked PDMS matrix at later stages of the reaction. Dreyer et al. also observed the presence of radicals within the PDA structure; which could also explain the fouling ability of the PDA species even at advanced reaction stages in the polymerization. The quality of the coating varies with the aging time, in addition to the stirring, being the coatings obtained at the early stages of the reaction smoother and more uniform than those obtained from later stages. This was expected given the formation of larger PDA aggregates as the reaction proceeds which become available to adhere to the substrates at later stages. Once again, the constant stirring of the reacting solution appeared to speed up the formation of larger PDA particles and simultaneously promoted the delamination of the deposits which resulted in rougher coatings than in the case of deposits from still solutions. The roughness analysis and SEM images of these surfaces are included (Figures S11 and S12, Supporting Information).

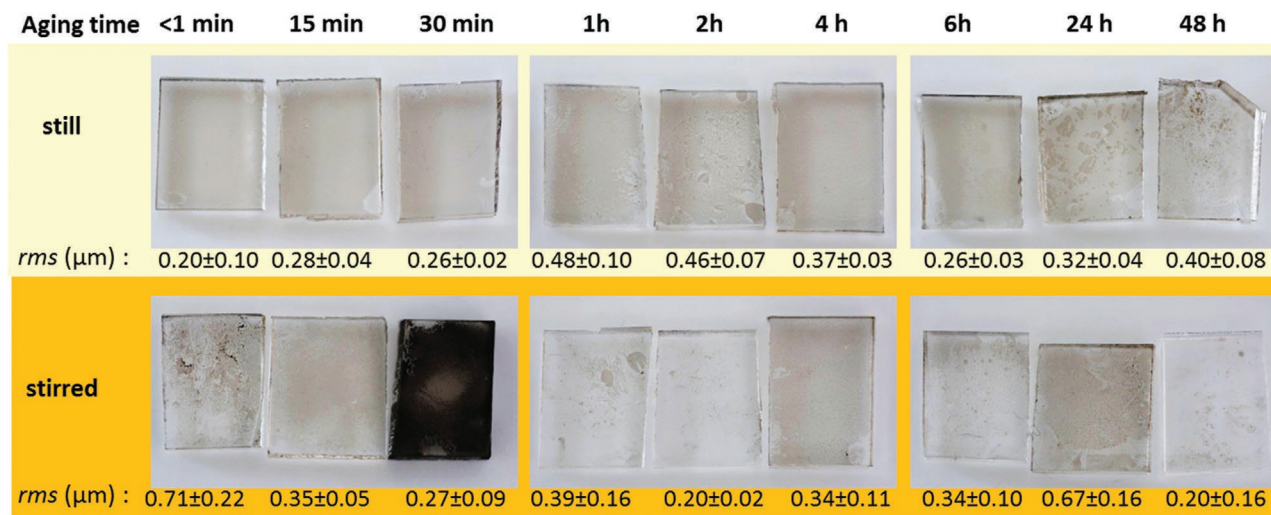


Figure 6. PDA coatings on SLIPS after 24 h of exposure to an aged PDA solution. Different SLIPS specimens introduced at increasing times from the beginning of the polymerization reaction of dopamine and remained immersed for 24 h.

2.5. Coating Mechanism

We theorized that the coating mechanism of PDA on SLIPS involved the formation of a complex of dopamine-silicon by initial interaction with the siloxane backbone of the Si-oil. This could facilitate the diffusion of the PDA aggregates through the lubricant layer till reaching the crosslinked PDMS matrix. There, the still active species could at first interact physically with the crosslinked matrix and then chemically. In order to elucidate this idea, three special reaction batches were prepared; the control batch contained the PDA solution with the standard preparation described in the Experimental Section, a second reaction batch had the similar preparation as the control PDA solution but with Si-oil in 50% vol., and the third reaction batch contained the control PDA solution with an immersed PDMS specimen (not swelled in Si-oil). These reactions were carried out under continuous stirring for 48 h. The solid products from these reactions were separated by centrifugation and washed with water three times, and then dried in vacuum before being analyzed by attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). The solids from the batch with Si-oil were additionally washed with hexane to remove the unbound oil. The ATR-FTIR measurements were done under vacuum and at room temperature to remove excessive environmental moist.

Figure 7 shows the comparison between the absorption spectra of the products from the three reaction batches, the spectrum of crosslinked PDMS is also included as reference. The principal absorption bands of PDMS are clearly evident in the spectra where the oxidative polymerization of dopamine is carried out in the presence of PDMS either crosslinked or un-crosslinked (i.e., Si-oil). These correspond to the absorption band at 2962 cm^{-1} from C–H stretching mode, those at 1258 and 789 cm^{-1} from the Si–(CH₃)₂ group, and that at 1011 cm^{-1} corresponding to the Si–O–Si group from the polymeric backbone (further details in Figures S13–S15, Supporting Information). These peaks are slightly shifted toward higher frequency and broadened. These observations are in agreement with a number of studies that suggest the depolymerization of PDMS in the presence of amines or at pH different from neutral.^[12] These evidences implied the creation of

covalent bonding between the polydimethylsiloxane units and the dopamine derivatives.

3. Discussion

In its initial polymerization stage, the small dopamine derivatives were in contact only with the outermost surface of the SLIPS formed by the unbound lubricant. Because of the low cohesion between lubricant molecules, the polymer molecules at the SLIPS surface were in a “free” state which renders an easy roll-off or detachment from the species landing on the surface. However, this was not always the case. Some aggregates could remain trapped within the lubricant layer and penetrate it until reaching the surface of the crosslinked PDMS. Despite the relative good chemical stability of PDMS, there are a number of studies that demonstrate the degradation of siloxanes under rather mild conditions.^[12a,d,i,j] The degradation through the cleavage of the backbone bond Si–O–Si is more likely to happen than through the removal of a methyl group given the lower energy barrier required. This bond cleavage can happen via a number of mechanisms which include aminolysis by primary and secondary amines with the aid of bases,^[12b–d] and alcoholysis^[12d,e] and hydrolysis,^[12f,g] both enhanced in the presence of acids and bases. All these processes occur by nucleophilic substitution which is more probable in the crosslinking sites because of the higher electrophilicity of tetra-functional silicon, in comparison to di-functional, due to the additional oxygen substituents. These reactions, however, are reversible and mostly limited to the surface; unless an external mechanism is provided to overcome the internal diffusion resistance of the hydrophobic PDMS matrix against the penetration of the activated nucleophiles.^[12d,h] Residual OH groups in the polymer could also promote the hydrolytic decomposition of PDMS.^[12i] Also, the presence of cations such as Na⁺, Ca²⁺, or Al³⁺ can enable the hydrolysis of the O–Si–O bond in PDMS.^[12j] Furthermore, oxidation to remove a methyl (CH₃) and replace it with a silanol (Si–OH) group, or to remove a proton on the methyl to form active radical species for anchoring silicone chain on PDA particles, can also take place in the presence

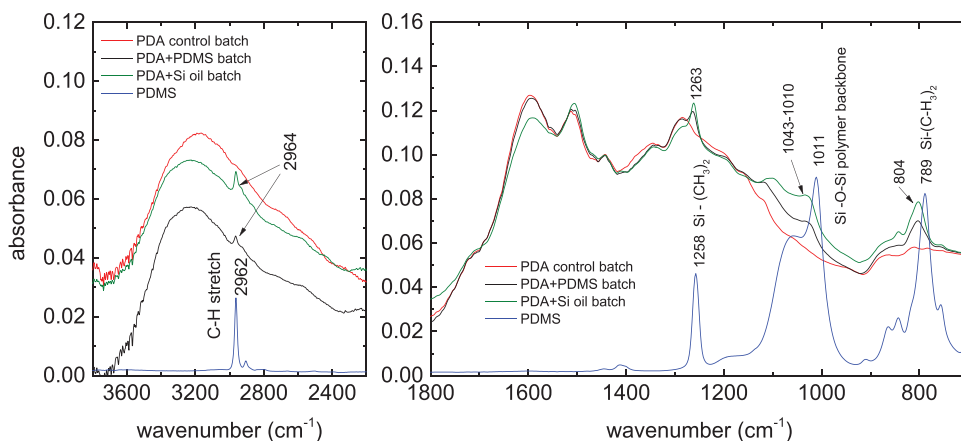


Figure 7. FT-IR spectra of PDA from control batch (red), from reaction batch with PDMS specimen (black), from reaction batch with Si-oil (green) and spectrum of pristine crosslinked PDMS (blue). Spectra obtained at room temperature and vacuum.

of radicals.^[12f] Overall, the active sites with potential interaction with siloxanes to cleave the bond Si–O are [–OH], [=O], [–NH] and radicals,^[12a] and all are contained within the PDA structure.^[3d] Therefore, the alkaline pH, the presence of Na⁺ cations in the coating solution together with the active sites present in the PDA structure, that is, [–OH], [=O], [–NH], and [–NH₂], and especially various radical species, provide the perfect condition for the cleavage of the Si–O bond or C–H bond and the subsequent anchoring of the dopamine/PDA species. Especially, the radicals formed in PDA particles are very active and might react not only with silicone but also with other lubricants or substrates.

Given the complexity of the coating solution formed by the changing dopamine species, more than one mechanism can explain the formation of these coatings. The multiple washing steps in different types of solvents with varying polarity demonstrated that the PDA coating was bonded to the crosslinked PDMS matrix and was not washed away when the lubricant was removed from the surface. Moreover, some PDA particles could be observed still on the substrate after the scratching test (Figure S11, Section 10, Supporting Information).

4. Conclusion

We have shown that despite the excellent medium-term functionality of various slippery systems, the extreme efficiency of the coating chemistry provided by the species from the oxidative polymerization of dopamine, appears to have supremacy in their encounter. In the in-depth study on silicone-based SLIPS systems, we have found that the coating versatility offered by the catechol and amine groups, plus all their derivatives, in addition to the presence of NaOH, undeniably renders the perfect coating scenario even for the most efficient antifouling surfaces thus far reported. The contaminating process might involve the formation of lubricant-containing active PDA particles which penetrate through the lubricant layer to bond on the substrate. Overall, we conclude that a thicker lubricant layer in SLIPS effectively extends the protection time against PDA fouling. However, the improved protection provided by the thicker lubricant layers in this study was also exceeded with the exposure of 24 h. On the other hand, the continuous stirring of the PDA coating solution in general accelerates the coating process. Since attached PDA can be easily modified with various species, our results imply a facile method to modify SLIPS or bond SLIPS coatings on substrates.

5. Experimental Section

Preparation of SLIPS: These membrane-based SLIPS were prepared with commercial PTFE (Sterlitech PTFE unlaminate membrane filter, 0.2 μm) and PP (Sterlitech PP membrane filter, 0.45 μm) membranes infused with either Si-oil with viscosity of 10 cSt (Sigma-Aldrich Chemie GmbH, Germany) or F-oil (DuPont Krytox 1506). The fluoropolymer matrix for the fluorinated-based SLIPS was produced with a UV-crosslinked mixture of perfluoropolyether (Flombin MD40, 75% wt, 226.4 mg), 2-(perfluorohexyl)ethyl acrylate (Fluorox Labs, USA, 24.75% wt, 74.7 mg), and 2-hydroxy-2-methylpropiofenone (Sigma-Aldrich Chemie GmbH, Germany, 0.25% wt, 0.75 mg). The fluoropolymer was immersed in the F-oil for 24 h before test.

Preparation of Silicon-based SLIPS: Commercially available PDMS (Sylgard 184 Dow Corning,) was used as the substrate to “fix” the lubricant by swelling. The substrates were prepared with a base to catalyst ratio 10:1 in weight. After mixing, degassing and baking at 70 °C overnight, the PDMS layers of about 1 mm in thickness were infused with the Si-oil until swelling equilibrium was reached (Figure S1, Supporting Information). The lubricant excess was removed by dabbing the specimens with a lint-free tissue. The specimens were used either immediately or after 2 days to allow the lubricant layer on the surface to reach its equilibrium thickness.

PDA Coatings: Commercial buffer solution (phosphate buffered saline 10× concentrate, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) was diluted in water to obtain the initial neutral solution with a phosphate buffer concentration of 0.01 M and a sodium chloride concentration of 0.154 M. A pH of 8.5 was achieved by addition of a NaOH; final concentration of about 15 mM NaOH. Dopamine·HCl (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany) was added to this basic solution in a concentration of 2 mg mL⁻¹ under continuous stirring. The specimens were placed in the solution immediately after complete dissolution of dopamine (≈7 s after initial addition of dopamine) or at specific increasing times after the reaction initiation. At this point the stirring was stopped for the coating condition named “still.” After a determined period between 1 and 24 h of continuous immersion in the stirred or still solution, the specimens were removed from the PDA solution and washed by pipetting distilled water to remove non-adhered PDA particles and carefully dried with air.

Surface Properties Measurements: The change in the hydrophobicity of the substrates was evaluated with a goniometer (OCA 25 DataPhysics Instruments GmbH, Filderstadt, Germany) using water drops of 3 μL. The contact angle was calculated in sessile mode using the provided software (SCA 20). The topography of the surfaces was analyzed with a white light interferometer (Zygo, NewView 5010, Middlefield, USA) which provided a 3D profile of the surfaces and also with SEM in low vacuum (Quanta 400 FEG D7953, FEI, Oregon, USA) which allowed simultaneous exploration of the elemental composition of the coatings by EDX (Genesis 2000, 10 keV, high vacuum). The thickness of lubricant films was estimated with an ellipsometer (M-2000DI, J. A. Woollan, Lincoln, USA) and using the optical parameters from Si-oil and PDMS measured separately with a refractometer (Abbemat MR MW, Anton Paar, Ostfildern, Germany).

ATR-FTIR Measurements: The chemical composition of the surfaces, coatings, reagents, and products was analyzed with an ATR-FTIR spectrometer (Vertex 70v, Bruker-Optik GmbH, Germany). This device was equipped with a vacuum unit and a golden gate to provide a condition of <1 hPa and heating up to 80 °C to ensure removal of the non-bound water from the highly hygroscopic PDA coatings.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

fouling, penetration, polydimethylsiloxane, polydopamine, slippery surfaces

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