Mechanical Stability of Liquid-Infused Surfaces Based on Mussel-Inspired Polydopamine Chemistry

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Liquid-infused surfaces exhibit remarkable repellency properties toward water, oils, and complex fluids and are widely applied to maintain clean, operational, and high-performing surfaces in various fields, from the biomedical sector to marine infrastructure. Polydopamine (PDA) forms an ideal base layer for the development of such coatings as it adheres to virtually any substrate and can be chemically modified via amino-containing molecules to adjust the surface properties. Here, strategies are explored to increase the mechanical stability of such coatings by i) incorporating imidazole during film formation to increase crosslinking, and ii) formation of a composite consisting of the organic PDA and an inorganic siliceous porous coating by infiltration of a preformed porous silica layer with PDA. Both strategies exhibit improved resistance to tangential shear assessed by a sandpaper abrasion test and to dynamic impact assessed by a sand trickle test. These improved mechanical properties are successfully transferred to liquid-infused surfaces created from such modified PDA base layers. The most durable coatings retain efficient liquid repellency after 25 abrasion cycles, indicating improved resilience in real-world applications.

1. Introduction

Creating surface properties able to provide resistance to marine biofouling,[1,2] bacterial biofilm formation,[3–5] ice adhesion,[6,7] or other forms of contamination[10,11] is of central importance in the design of functional coatings. Liquid-infused surfaces (LISs) inspired by the Nepenthes pitcher plant,[12] have shown promising performance in all these areas due to the presence of a thin liquid layer, termed lubricant, covering the underlying surface.[13–16] This layer prevents direct contact of contaminations with the underlying solid and, due to its liquid nature, enables efficient self-cleaning properties.[13] In general, three different approaches have been developed to fabricate LISs: surface functionalization of a porous solid substrate and subsequent infiltration to form slippery liquid-infused porous surfaces (SLIPS),[13] chemically anchoring lubricant materials to the surface in the form of grafted polymer brushes,[17,18] or the use of swollen organogels.[19–22]

In the design of LIS coatings, the choice of substrates is often limited due to the selectivity of typical anchor groups needed to provide the required surface functionalization to minimize the interfacial energy with the lubricant and thus form a stable coating.[11,13] A versatile strategy to create LIS coatings independent of the material employs a mussel-inspired chemistry. The mussel foot proteins are known to contain L-3,4-dihydroxyphenylalanine (DOPA) and lysine,[23] which are responsible for surface adhesion even underwater.[24] The mussel-inspired surface chemistry has been applied for material-independent surface modifications for example in the form of catecholamines.[25–28] Dopamine is an example of catecholamines, which polymerizes oxidatively forming a thin polydopamine (PDA) film on a broad range of substrate materials,[29–31] and has been successfully implemented in various coatings strategies, but also shows catalytic activities.[32] Importantly, the PDA coating can be surface functionalized due to its remaining reactivity toward nucleophiles such as amines, thiols and imidazoles.[33–35] This, in turn, allows the substrate-independent formation of LIS coatings: First, the PDA base layer is formed by the oxidative polymerization of PDA on a desired surface. Second, the PDA is surface functionalized via reactive functional groups to match the interfacial energy of the coating to a desired lubricant. Finally, the lubricant is infused to form a LIS.[25] Optimization of this reaction pathway also enabled the combination of these reactions into two and one-step processes...
As an example of the broad applicability of the PDA-based system in real-world scenarios, we previously coated elastomeric shoe soles, which showed a significant decrease in cement adhesion (Figure 1b, c) \[36\] compared to the uncoated reference.

Here, we explore the mechanical stability of PDA-based liquid-repellent coatings. This stability is an important, yet often underestimated aspect of repellent coatings in real-world scenarios, where surfaces are subjected to impact, wear, or cleaning procedures. We first focus on enhancing the mechanical stability of the bare PDA coating and subsequently transfer the knowledge to the LISs systems based on PDA. In this context, pure PDA coatings can exhibit elastic moduli in the range of 2–3 GPa. \[37,38\]

In general, there are various strategies to enhance the mechanical properties of PDA: the increase of intrinsic PDA crosslinking by thermal \[37,39\] or laser \[40\] processes; extrinsic PDA crosslinking with primary amines \[41,42\] and multi-amines \[43–46\] by incorporation of ions \[38\] or inorganic non-metallic particles \[43,47\]. We focused on two distinct strategies to enhance the mechanical stability of PDA: the increase in the degree of crosslinking by the addition of imidazole as a nucleophile, and the addition of inorganic particles to form a composite material \[43,47\]. We focused on two distinct strategies to enhance the mechanical stability of PDA: the increase in the degree of crosslinking by the addition of imidazole as a nucleophile, and the addition of inorganic particles to form a composite material \[43,47\].

In this article, we pursue and compare both strategies to improve the mechanical resistance of the PDA base coatings against mechanical impact and scratch resistance.

2. Results and Discussion

Figure 2a–d schematically illustrates our approaches to increase the mechanical stability. The reference sample consists of the PDA coating on a flat substrate (Figure 2a). The enhancement of mechanical stability was addressed via the formation of an organic–inorganic composite (Figure 2b), the increase of crosslinking within the PDA (Figure 2c), and the combination of both (Figure 2d). The composite structure was formed by the deposition of a uniform, porous layer of silica nanoparticles via dip-coating \[57\] and subsequently coating the voids in the inorganic matrix (Figure 2d). \[36\] Scanning electron microscopy (SEM) cross-sectional analyses (Figure 2e) show the porous nature of the initial porous silica substrate. A thickness of the porous coating of \(\approx 100\) nm can be seen. Upon addition of the PDA layer, the porous film appears completely filled by the PDA coating, evidenced from the absence of visible holes and a blurring of the image characteristic of soft polymer layers (Figure 2f). The film thickness only marginally increased. While it was not possible to directly quantify the layer thickness of the deposited PDA film, previous results from our group of similar coating processes on flat substrates shows a PDA layer thickness of \(\approx 25\) nm \[36\] in agreement with the visual impression of the SEM cross sections.

To increase the crosslinking density in the PDA film, we added imidazole during the oxidative polymerization in equivalent molar ratios to the monomer dopamine HCl (Figure 2c, d). The addition and the choice of imidazole molecules was inspired by the biological crosslinking processes, in which the imidazole group in histidine reacts with catechol groups \[48,49,53–56\].
The formation of a PDA film is often investigated by UV–vis.\textsuperscript{58} In the case of plain PDA, it has been shown that the natural crosslinking reaction extends the $\pi$-system, which in turn, increases the absorption.\textsuperscript{58} Since we could not directly observe the presence of the imidazole moieties spectroscopically, we indirectly assessed its presence by a decrease in UV–vis transmission (Figure 2g, h) compared to plain glass. A further decrease compared to plain PDA therefore suggests the incorporation of imidazole and the extension of the conjugated $\pi$-system.

2.1. Mechanical Resistance to Linear Abrasion of PDA Coatings

We first compared the stability of the different coatings against linear abrasion.\textsuperscript{59} To this end, a defined weight of 100 g with a diameter of 21.4 mm was placed on top of a sandpaper (7000 grit) and then manually pulled over the coated substrates (76x13 mm) for 50 cycles (Figure 3a).\textsuperscript{59,60} To assess the resistance of the coating, we took advantage of the broadband absorption of PDA, which is responsible for the brownish color of the coatings (Figure 2g, h). Upon removal of the PDA, the light transmission consequently increases. Therefore, we used the difference between transmission before and after abrasion as a measure to assess the damage to the PDA coatings (Figure 3b; Table S1 and S2, Supporting Information). We supplemented this macroscopic analysis with microscopy images to directly reveal the mechanical damage of the coatings (Figure 3c).

The combination of PDA and porous coating reduced the change in light transmission from 16.3 ± 0.7 % for the reference PDA coating to 1.2 ± 0.8 %, indicating that the scratch resistance was significantly enhanced (Figure 3b). The incorporation of imidazole into the PDA coating similarly reduced the change in light transmission, albeit to a lesser extent (11.0 ± 2.2 %). The lowest change in light transmission was observed for the...
imidazole-containing PDA layer within the porous silica matrix (0.9 ± 0.2 %). The optical microscopy images follow the macroscopic trends and show that the reference PDA coating is almost completely removed, while the composite consisting of the porous coating remains largely on the substrate. This is true for both the PDA and imidazole-containing PDA. (Figure 3c, note that in the images, the darker regions represent the abraded parts of the coatings).

2.2. Mechanical Resistance to Dynamic Impact of PDA Coatings

Besides abrasion by scratching, a typical mode of mechanical damage is the dynamic impact of solid material onto the coating.[60] We simulated such wear scenarios using a sand trickling test, inspired by a standardized protocol (DIN EN 168:2002-04). In this test, the substrate is placed at an angle of 45 ° and dynamically impacted with 3 kg of sand (grain size 0.5 – 0.71 mm) falling from a height of 1.725 m through two sieves (12 mesh size) (Figure 4a).[60]

In this case, the change in light transmission cannot be used as a direct measure of the removal of the coating, because light scattering arising from the collisions changes the transmissivity so that even a glass reference sample would exhibit a different transmission. To circumvent this issue, we used the haze factor as a metric to indirectly assess the damage to the coating (Figure 4b,c). The haze factor describes the amount of scattered light relative to the amount of transmitted light passing through a sample (Table S3, Figure S7, Supporting Information).[61,62] Therefore, any damage to the substrate that contributes to scattering will directly increase the haze factor.

As reference samples, we used a pristine glass slide and a glass slide coated with the porous silica layer shown in Figure 2a,b. The uncoated flat substrate shows a lower transmission compared to the uncoated porous coating (Figure 2g,h, T2 in Figures S1 and S4, Supporting Information). The increase of diffuse transmission after sand trickling was lower for the porous coating (T4 in Figures S1 and S4, Supporting Information). The addition of PDA onto a flat glass substrate decreased the haze factor from 15.4 ± 2.2 % to 8.6 ± 0.8 %, which further reduced to 7.1 ± 0.7 % when imidazole was incorporated into the PDA coating (Figure 4b, Table S3, Figures S1–3, Supporting Information). The composite consisting of the porous coating and PDA showed a haze factor of 5.3 ± 0.6 % and the lowest haze factor of
4.4 ± 0.1% was obtained for the imidazole-containing PDA layer integrated into the porous SiO₂ coating.

The PDA coated flat substrate with and without imidazole shows a higher transmission compared to the PDA coated porous coatings (Figure 2g,h, T2 in Figures S2 and S5, Supporting Information). Furthermore, the increase of diffuse transmission after sand trickling was lower for the PDA porous coating compared to the PDA coated flat substrate (T4 in Figures S2 and S5, Supporting Information). This lower change in haze value matches with the observation of less damage in the optical microscopy images (Figure 4c). Inorganic porous films can show flexibility, which may cause deformation instead of destruction, resulting in a lower increase of the haze value. The flexibility of porous coatings can be measured via nanoindentation. Individual microscopy images of the different samples after the sand trickling tests (Figure 4c, Table S3, Figures S1–6, Supporting Information) reveal impact damages of all coatings, perhaps with smaller numbers of impact points for the composite coatings. The large scatter in data of individual images prohibits a clear comparison. Based on the macroscopic investigation via the haze factor, an increase in impact resistance is evidenced, with the observation of less damage in the optical microscopy images (Figure 4c). Inorganic porous films can show flexibility, which may cause deformation instead of destruction, resulting in a lower increase of the haze value.

2.3. Mechanical Resistance to Linear Abrasion of Liquid-Infused Surfaces (LIS) based on PDA

Having optimized the mechanical resistance of the PDA coatings, we used these coatings as a base layer for the design of liquid-infused surfaces (LISs). To this end, we applied a self-functionalizing strategy recently developed in our laboratory and added a thin layer of the silicone oil used as the lubricant. This layer contained monoaminopropyl-terminated polydimethylsiloxane (MAP-PDMS) as a reactive species, which reacted with the underlying PDA base layer and thus minimized the lubricant/substrate interfacial energy in situ during incubation. To ensure proper functionalization and repellency performance of the LIS systems, we allowed the lubricant to sit on the substrate for 80 h.

We assessed the mechanical stability by performing linear abrasion cycles using the same methodology as for the pure PDA base layers (Figure 3). We measured the water contact angle hysteresis (CAH) and the sliding angle (SA) for all different LIS systems with increasing abrasion cycles (Figure 5a,b). A coating was classified as slippery (i.e., retaining the liquid repellency properties) if CAH and SA remained below 10, using a conventional definition for repellent coatings. Pinned droplets on failed substrates typically exhibited very large CAH and SA values, or did not slide from the substrate at all. These samples were indicated as arrows in Figure 5a,b.

The reference LIS system based on untreated PDA lost its repellent properties after 5 abrasion cycles (Figure 5a,b, green triangles).

Using the imidazole-modified PDA coatings as the base layer for the LIS improved its wear resistance. This type of LIS only lost its repellency properties after 25 abrasion cycles (Figure 5a,b, gray triangles). The large deviation of the CAH might indicate a decrease of liquid repellent properties.

LIS based on the PDA on a porous coating layer also improved the resistance against linear abrasion and retained repellency properties up to 10 abrasion cycles (Figure 5a,b, red squares). Noteworthy, however, these coatings failed before the imidazole-containing LISs. This contrasts the behavior of the pure base layers, where the incorporation into the porous matrix tended to show superior mechanical properties. We hypothesize that this difference in behavior is related to partial swelling of the PDA layer upon long-term exposure to silicon oil. In this case, the increase in chemical crosslinking may even more efficiently hinder such swelling and therefore creates a more mechanically robust coating.

The best performance was achieved with the imidazole-containing PDA on a porous coating layer, which retained a very low CAH of 1.9 ± 1.6° after 25 abrasion cycles (Figure 5a,b, blue spheres). Notably, in these experiments, the fluid nature of the lubricant can re-infiltreate into defects within the underlying coating, providing self-healing characteristics. However, this

![Figure 4](image-url)
ability is eventually compromised once the crack density becomes too large for a given lubricant thickness. In our case, all experiments were performed without replenishing lubricant. The enduring performance despite partial removal of the lubricant by the sandpaper supports the real-life performance of such coatings and could even be extended by a lubricant replenishing step.

3. Conclusion

In conclusion, we investigated the mechanical properties of PDA-based coatings with two different strengthening mechanisms. Enhancing chemical crosslinking and the creation of a composite consisting of the porous coating and PDA both increased the resistance to linear abrasion and dynamic impact. The best results were found for a combination of both strategies, obtained by porous silica coating with imidazole-containing PDA. The increased resistance to mechanical damage was successfully transferred to PDA-based LIS coatings, opening the way toward enduring performance of liquid repellent, anti-fouling, and self-cleaning materials. Based on the enhanced performance of such coatings demonstrated in this manuscript, future fundamental research should focus on the detailed characterization, the mechanistic understanding and the quantification of the imidazole incorporation, and the influence of pore sizes and coating thickness of the inorganic matrix on the mechanical properties.

4. Experimental Section

Materials: Glass substrates (soda-lime glass slides, 76x13x1 mm) were purchased from Thermo Fischer. Dopamine HCl (≥ 98 %, Sigma-Aldrich), triethylamine (99 %, Sigma-Aldrich), imidazole (≥ 99%, Carl Roth), tri(hydroxymethyl) aminomethane (TRIS, ≥ 99.9%, Carl Roth), monoaminopropyl-terminated polydimethylsiloxane (MAP-PDMS, MCR-A11, ≥ 95 %, Gelest Inc.), silicone oil (10 cSt, Sigma Aldrich), Levasil® CS30-716 P (Kurt Obermeier), RBS 50 (Carl Roth), phosphoric acid (85%, AppliChem GmbH), ethanol and isopropanol (Sigma Aldrich) were used as received. All water was double-filtered and deionized (DDI, 18.2 MΩ cm resistivity, Purelab Flex Z, ELGA Veolia).

LIS Fabrication Procedure with In Situ Self-Functionalizing Lubricants: PDA Coating: The glass substrates were cleaned by ultrasonication at 80 W for 5 min in water, ethanol (denaturated, Carl Roth), acetone (≥ 99.5 %, Carl Roth), subsequently dried in air at room temperature and further cleaned with oxygen plasma (Diener electronics, model Femto SLS) for 5 min at 100 W at 0.2 mbar oxygen before PDA coating. The PDA coating was carried out according to the literature. Briefly, an aqueous dopamine solution was prepared by dissolving dopamine HCl (1 g L⁻¹) and TRIS (10 mM) in DDI water at pH 8.5. The substrates were placed vertically in a glass vial with 40 mL of the dopamine solution and left to react 24 h at room temperature. Afterward, the samples were extensively rinsed with DDI water and dried in air at room temperature.

In situ self-functionalizing process: The LIS fabrication with in situ self-functionalizing lubricants was performed according the procedure of Chiera et al.[36] Briefly, the reactive species (MAP-PDMS, 20 mM) and TEA (20 mM) were dissolved in silicone oil and added to the PDA coating with a surface coverage of ca. 15 μL cm⁻². Excess oil was removed by placing the substrate vertically for 10 min prior testing.

Fabrication of porous coatings: The porous coatings were fabricated by a dip-coating process with a sol-gel procedure. A sol was fabricated as described in European Patent Specification EP 3 176 229 B1.[67] The primary particle size of the sol was 15 nm. The glass substrates were stored overnight in a 10 % aqueous solution of RBS 50 (Carl Roth). After incubation overnight, the substrates were rinsed with deionized water and stored for 5 h in 10 % phosphoric acid. Afterward, they were rinsed again with deionized water and dry-blown with oil-free compressed air. The substrates were dip-coated with a withdrawal speed of 100 mm min⁻¹. After drying at room temperature, the coated substrates were placed in a vented furnace (Heraeus Instruments K 750/2) at room temperature and heated to 500 °C with a heating rate of 5 K min⁻¹. The temperature was held at 500 °C for 30 min and afterward, the oven was allowed to cool down to room temperature overnight.

Characterization of the Coatings: Wettability: The surface wettting behavior was investigated with a contact angle measurement device (Dataphysics OCA) and the manufacturer’s software (SCA202 V 3.50.1). Water droplets of 4 μL (Milli-Q grade) were dispensed from a glass syringe equipped with a 0.5 mm needle. At least 8 droplets were measured and averaged for the contact angle (CA) measurements. The contact angle hysteresis (CAH) measurements were performed three times with 8 μL water droplets and a tilting device. The sliding angles (SA) were determined with the software ImageJ 1.52p.

Figure 5. Mechanical stability of liquid-infused surfaces (LIS) based on a PDA base layer, assessed by linear abrasion with sandpaper (7000 grit) and 100 g abrasion weight. a) Contact angle hysteresis (CAH) b) and sliding angle (SA) of the different PDA-based LISs systems as a function of the number of abrasion cycles. The LIS coatings were prepared on a flat substrate with PDA (green), and imidazole-containing PDA (blue). The dotted line at 10° indicates the threshold values for CAH and SA for a surface to be classified as slippery. c) Images of sliding water droplets on a LIS based on the imidazole-containing PDA on a porous coating after different abrasion cycles. Note that the arrows indicate data points where the samples were not presenting slippery and liquid repellent properties, and the values of CAH and SA were out of range of the axes.
Surface analysis: The surface was characterized by scanning electron microscopy (SEM, Zeiss AG; Gemini 500) with an accelerating voltage of 3.0 kV, a 10 μm aperture, and an InLens detector. The samples were sputtered with Pt before the SEM analysis.

Linear abrasion test: The procedure for testing tangential shear via linear abrasion was adapted from Schlaich et al.[68]. Briefly, a grinding medium (7000 grit from Starcke) was placed on a sample slide on a surface of ca. 13×76 mm². The coating of the sample slide was facing upward, and the grinding paper downside. A weight (100 g) with a diameter of 21.4 mm was placed on top of the grinding paper to ensure a constant shear force during the shearing process. Moving the sandpaper once over the coating in one direction was defined as one cycle. Figure 3a shows the schematic and the experimental setup of the linear abrasion test. The abraded samples were characterized by UV–vis transmission (Lambda 950, PerkinElmer) in the wavelength range from 400 to 800 nm before and after the abrasion. The surfaces were analyzed by optical microscopy (Ergolux, ErnstLeitzWetzler, model 020–448,026) at a 16x magnification, and the images were taken with a CMOS camera (Thorlabs, type DCC3260C). Dynamic impact test by sand trickling: The dynamic impact durability was performed via sand trickling test according to DIN EN 168:2002 04[69] by letting 3 kg of sand (particle size 0.5–0.71 mm, Buschquarz) trickle from a height of 1.725 m through two sieves with 12 mesh size onto the samples placed at an angle of 45°. The complete sample surfaces of the microscope glass were investigated by optical microscopy. The optical properties of the samples before and after abrasion were investigated via the haze measurements, where a UV–vis spectra with an integrating sphere with a 15 cm diameter was recorded in the wavelength range between 400 and 800 nm to follow the standard ASTM D1003-21 (see Figure S7, Supporting Information).[70] Figure 4a shows the schematic and the experimental setup of the dynamic impact test.

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.

Author Contributions

S.C. and M.G. contributed equally to this work. S.C. and M.G. performed the experiments and developed the characterization methods for testing the mechanical resistance of the PDA coatings. P.L. and C.S. developed and supervised the sol-gel process for the porous coatings. T.Z. synthesized the sol and fabricated the porous coatings via dip coating and sol-gel procedure. S.C. coated the porous coatings with PDA. S.C. converted the flat and porous PDA-coated glass substrates into LISs via in situ self-functionalizing lubricants. S.C. and M.G. tested the mechanical resistance to linear abrasion of the flat and porous LISs. S.C., S.W., N.V., and K.M. supervised the project. S.C., T.Z., M.G., and N.V. wrote the manuscript. All authors discussed the results, revised them, and contributed to the final manuscript.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords

coatings, liquid-infused surfaces, mechanical resistance, polydopamine, wetting, coatings

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