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RESEARCH ARTICLE

PLASMA PROCESSES AND POLYMERS

Wetting behavior and stability of surface-modified polyurethane materials

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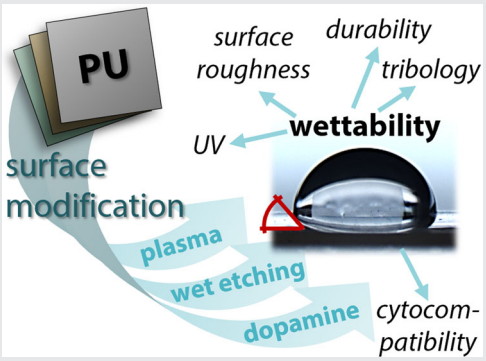
Abstract

Even though polyurethanes (PU) constitute a class of highly versatile and customizable polymeric materials, being able to modify their surface properties, for example, their wettability, without altering the composition of the bulk material would often be desirable. However, PU-based materials can be both rather diverse and resilient to chemical modification. Thus, in this study, three PU variants are subjected to three different treatments that aim at altering the wetting properties of the materials: We assess the feasibility of plasma treatment, dopamine incubation, and chemical etching, and evaluate the stability of the obtained surface modifications with regard to wet and dry storage, UV exposure, and application-specific properties such as lubricity and colonization with eukaryotic cells. The results obtained here can be used to achieve an additional customization of PU surfaces to tailor their behavior for selected applications where dedicated surface properties are required.



KEYWORDS

dopamine deposition, oxygen plasma treatment, polyurethanes, surface modification, water contact angle

1 | INTRODUCTION

The term polyurethane (PU) summarizes a large range of versatile and structurally diverse materials. Most PUs show interesting mechanical, physical, and chemical behaviors, and they can combine competing properties such as high robustness and strong flexibility. A chemical feature that all these materials share is a urethane group (–NH–CO–O–) as the major repeating motif in their backbone structure. To fit different requirements, PU-based materials can be tailored in terms of chemistry (by varying the type and degree of cross-linking) and appearance (they can be manufactured into solid materials, soft/hard foams, foils, adhesives, and coatings);

accordingly, the range of applications that PU materials can be used for is vast[1]: Examples range from technical applications in automotive and (aero)nautic industries (e.g., seating, instrument panels, chemically resistant/protective coatings),[2] over building and construction applications (e.g., thermal and acoustic insulators, floors, multi-material glues),[3] and everyday products (e.g., shoe soles, cushions)[4] to single-use (e.g., wound dressings, urinary catheters, hemodialysis tubes) and high-performance medical devices (such as cardiovascular implants).[5]

In some of these applications, a good interaction of the material with an aqueous environment, that is, hydrophilic properties, would be desirable. In biomedical applications, good wetting behavior is often related to, for example, enhanced interaction with cells and good biocompatibility of the material.[6] For technical and industrial applications, good interactions of polymeric materials with aqueous solutions are often required when preparing them for printing or coating and/or to improve their adhesive properties for optical, protective, or other functional layers/additives.[7]

However, as PU variants can be rather hydrophobic, this calls for a modification process that maintains the other highly interesting properties of PU materials. Accordingly, surface modification procedures appear to be most suitable to achieve this goal—altering the chemical properties of the PU polymers themselves before material generation would be likely to change the bulk behavior of the materials as well, and this is not desired.

A range of surface treatment procedures for polymeric materials have been reported in the literature; among those, some of the most prominent strategies are plasma treatment, chemical etching, and dopamine treatment. The phrase "plasma treatment" summarizes numerous methods/processes that generate (partially) ionized gas and/or radicals, which are frequently applied to various materials for surface modification, for example, for surface hydrophilization.[8,9] However, plasma processes often require specialized devices to provide either low ambient pressure (or even vacuum)[8] or high treatment temperatures (greater than or equal to several hundred degrees Celsius)[9], and these harsh conditions are not always suitable. For instance, when the inside of a hollow, flexible sample (like a balloon) or temperature-sensitive materials (i.e., most polymeric materials based on, e.g., polymethylmethacrylate, polystyrene, or polyvinylchloride) is to be treated, a different approach needs to be chosen. Similarly, for complexly shaped or porous samples, achieving a homogenous plasma treatment of the whole surface can be difficult,[10] especially when short exposure times (~10 s to 5 min), as typical for plasma activation of (polymeric) surfaces, are selected.[11] Conversely, longer exposure times can lead to undesired etching effects becoming dominant on the surfaces,[12,13] which can induce damage, especially to fragile objects or thin structures.

A second strategy to hydrophilize the surface of a material, which, in terms of its mechanistic working principle, is closely related to plasma activation, is chemical etching with fluids. Here, the samples are exposed to certain aggressive basic or acidic solutions, which modify the surface by creating new functional groups. Thus, similar to plasma treatment, also here, suitable conditions need to be identified that achieve the desired surface activation without damaging the material.[14]

Such issues should, however, not occur when dopamine treatment is used to alter the surface properties of a material. This solution-based, additive process was first introduced in 2007.[15] Here, under atmospheric conditions, dopamine molecules polymerize in basic solutions (pH ~8.5) and this leads to the deposition of a thin layer of (poly)dopamine onto the surface of a material exposed to such a dopamine solution. Even though the detailed mechanisms driving this layer formation are not fully understood yet (despite extensive studies),[16,17] it was shown that this strategy can be successfully applied to a broad range of materials including metals, glass, ceramics, and different polymeric materials.[15]

Here, we show that the efficiency of different surface modifications, which aim at improving the interaction of PU materials with aqueous solutions, varies with the type of PU. We compare the effect of plasma treatment, chemical etching, and dopamine treatment on the wettability of the different materials and evaluate the stability of these treatments after material storage under selected conditions. Additionally, the treated samples are evaluated after certain application-related challenges, that is, after disinfection with UV light, colonization with eukaryotic cells, and exposure to tribological load. Our results show that, depending on the desired application area, different surface treatment variants can fulfill the desired requirements for the PU materials tested here.

2 | EXPERIMENTAL SECTION

2.1 | PU materials

In this study, three different kinds of PU samples were investigated: first, the technical, elastomeric polyurethane THOMAPLAST®-PUR (PUR; Reichelt Chemietechnik GmbH + Co.) and second, two medical-grade polycarbonate-based thermoplastic PUs: the aliphatic Carbothane™ PC-3575A (PC; Lubrizol Advanced Materials [LAM]) and the aromatic Carbothane™ AC-4095A

(AC; LAM). PUR samples were commercially available in flat sheets with a thickness of 2 mm. In contrast, the material samples obtained from LAM had the form of thin, extruded films (thickness: 176 μm for PC and 250 μm for AC). These samples were provided to our project partners at the Fraunhofer Institute for Manufacturing Engineering and Automation who forwarded them to us to conduct surface modification tests with.

For cell culture tests and tribology measurements, round samples with diameters of 6 and 7 mm, respectively, were prepared. For all the other tests, rectangular samples with a size of ~1 cm^2 were used. Before any tests, all samples were thoroughly cleaned with 80% ethanol (EtOH; Carl Roth GmbH + Co. KG) and ultrapure water (ddH_2O), and then dried at room temperature overnight.

2.2 | Surface modifications

Three different surface treatment strategies were applied to improve the wettability of the materials and thus to enhance their performance for applications in aqueous environments.

2.2.1 | Oxygen plasma treatment

For plasma treatment, a commercial plasma system (Femto Model 1 base unit type B; Diener electronic GmbH & Co. KG) was used to facilitate the reproducibility of the process. This device uses a reactive-ion etching system to generate plasma at low pressure and ambient temperature; the usable power ranges from 0 to 100 W at a generator frequency of 40 kHz, and the cylindrical vacuum chamber has a volume of ~2 L. For treatment, the samples (prepared as described under Section 2.1) were placed onto a glass specimen carrier to (electrically) isolate them from the rest of the vacuum chamber. The chamber was then evacuated for ~5 min, and the desired low pressure of 0.4 mbar was obtained by manual adjustment via a needle valve. As the PU samples were—for practical reasons—simply dried under ambient conditions and the low pressure was established comparably quickly, the occurrence of residues of atmospheric air or water within the chamber or on the sample surface cannot be fully excluded. Then, the chamber was flushed with oxygen and the plasma was ignited. Based on a previously published process[18] used to activate different polymeric materials, plasma was generated for 90 s using the above-mentioned parameters. During this time span, fresh oxygen was constantly provided and ionized, and the used plasma/gas was removed by the vacuum system to maintain a steady and sufficient amount of unreacted oxygen plasma. The treated samples were used directly once the plasma treatment process had finished. Only the upper sample surfaces, where the nonpolar methyl groups could be reached by the plasma and thus converted into (mainly) hydroxy groups, were used for any further investigations.

2.2.2 | Dopamine treatment

For dopamine treatment, 0.4% (w/v) dopamine hydrochloride (Sigma-Aldrich Inc.) was dissolved in a buffer solution containing 20 mM HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; Roth) and 154 mM sodium chloride (NaCl; Roth) adjusted to a pH value of 8.5. Under basic pH conditions, dopamine immediately starts to polymerize and deposit/adhere onto contact surfaces; this property can be used to generate a polydopamine layer on a broad range of materials by simply immersing the object into such a dopamine solution. Here, for practical reasons, always two samples (with their back sides aligned) were placed—standing upright—into a well of a 48-well plate. Then, the well was filled with ~1 ml of the dopamine solution until the samples were entirely covered. Subsequently, the samples were incubated on a slowly moving tilting shaker at room temperature for 3 h. Afterward, unbound dopamine molecules were removed by rinsing with ddH_2O, and the dopamine-treated samples were either directly used (if "wet" storage conditions were analyzed) or dried at room temperature overnight (if "dry" storage conditions were tested).

Since polydopamine tends to agglomerate into big particles (with sizes up to several micrometers), this could lead to inhomogeneous layers on the material surfaces and thus to unreproducible behavior of dopamine-treated samples. To avoid this, two different strategies were implemented here. First, as polydopamine agglomeration is a time-dependent process, the degree of dopamine polymerization was minimized by shortening the storage time of freshly prepared dopamine solutions as much as possible; this was achieved by dissolving the dopamine just before use (in this manuscript, this approach is referred to as "dopa-direct"). However, in such a short time, a fully homogeneous dopamine solution cannot be generated; because of this, variations in dopamine concentrations between different wells cannot be ruled out. The second approach is based on the scientific consensus that dopamine polymerization is initiated by oxidation processes.[19] Accordingly, here, we limited sample access to atmospheric oxygen. To achieve this, the incubation container was completely filled with the dopamine solution and the

container lid was closed and sealed with a laboratory film. Then, overnight incubation was conducted to allow the solution to equilibrate, while minimizing dopamine polymerization processes (in this manuscript, this approach is referred to as "dopa-overnight").

2.2.3 | Chemical etching

To chemically etch the material surfaces of the three PU variants tested here, each sample was completely immersed into the designated, concentrated acidic solution for 1 min at room temperature. The acidic solutions used here were 96% sulfuric acid (H_2SO_4; Roth) and 65% nitric acid (HNO_3; Roth). Consecutively, the etching reaction was interrupted by dipping the sample into 1 M sodium hydroxide (NaOH; Roth) and rinsing it with ddH_2O. For the subsequent surface analysis tests, the back sides of the samples were dried on a lint-free laboratory wipe; then, the samples were placed onto a glass slide with those back sides facing down.

In addition, as PC and AC are polycarbothane-based materials, for which the literature suggests that NaOH could be a suitable etching medium,[20] 32% NaOH was tested as well. Here, the same technique was used as that described for acidic solutions above, except that 1 M hydrogen chloride (HCl; Roth) was used to interrupt the etching reaction.

Furthermore, the literature suggests that etching of different materials can also be achieved by a mixture containing both an acidic solution and an oxidizing agent.[21] Here, such a mixed solution was prepared by combining 17.8 M H_2SO_4 and 11.6 M hydrogen peroxide (H_2O_2; Merck Chemicals GmbH) in a volume ratio of 3:1, which results in a very aggressive liquid known as "piranha solution." However, as the exposure of the examined materials to such a concentrated piranha solution entailed immediate and direct disintegration of the materials, the samples were instead treated with a diluted piranha solution, based on 5 M H_2SO_4, under constant stirring at 40°C for 5 h.

2.2.4 | Dry and wet reference samples

Here, as we compare a dry surface treatment (plasma treatment) with solution-based surface treatments (dopamine treatment/chemical etching), there are also different control groups to consider to ensure comparability. As "dry reference" samples, pristine, completely untreated materials are used. These serve as reference points for plasma-treated material samples characterized directly after this treatment, or for such samples treated with aqueous solutions, which were dried at room temperature overnight before characterization. In contrast, "wet reference" samples are untreated material samples that were immersed into distilled water for 3 h (this corresponds to the incubation time used for dopamine treatments). Such "wet reference" samples were used as reference points for all other conditions studied here.

2.3 | Storage conditions for stability tests

In addition to assessing the behavior of the PU samples immediately after surface treatment, the durability of the surface treatment was examined as well. Here, once more, two different storage conditions were compared: First, storage under wet (roughly physiological) conditions. Here, each sample was placed into a 24-well plate and the well was filled with 1 ml of Dulbecco's phosphate-buffered saline (DPBS; Sigma-Aldrich). Then, the well plate was stored in an oven at 37°C while avoiding evaporation. The second set of storage tests was conducted under dry conditions. Therefore, samples dried overnight were placed into a 24-well plate, which was stored at 7°C.

2.4 | Surface analysis

2.4.1 | Contact angle (CA) measurements

To determine the wetting behavior of the different PU variants before and after surface treatment, CA measurements were conducted. Therefore, samples were first gently cleaned and dried with particle-free pressurized air. Afterward, a droplet of 8 µl of ddH_2O water was placed onto each sample, and a transversal image of the liquid–solid interface was captured using a high-resolution camera (Point Gray Research). Then, the static CA value was determined using the software ImageJ and the "drop snake" plug-in (both open-source).

2.4.2 | Confocal laser scanning microscopy

Confocal laser scanning microscopy was conducted using a VK-X1000 microscope (Keyence) equipped with a ×50 lens (NA = 0.95; Nikon). Also, here, before performing measurements, all samples were gently cleaned and dried with particle-free pressurized air. Then, the samples were placed onto a glass slide using a droplet of 50 µl of distilled water as a thin spacer. This was necessary to allow the measuring device to automatically differentiate

between the very thin, transparent Carbothane foils and the glass slide. For each material/treatment combination, at least three samples were examined. On each sample, a stitched image was acquired such that a total area of 0.56 mm^2 could be analyzed. For this analysis, the software MultiFileAnalyzer (Keyence) was used. First, sample waviness (a wave form with correction strength 4 out of 20) and a linear tilt were removed from the topographical images. Additionally, to eliminate artifacts originating from the transparent nature of the samples (i.e., unrealistically deep valleys), the obtained profiles were inverted, a height cut (weak level) was applied, and the profiles were inverted back to the original configuration. From the adjusted topographical images, the metrological parameter S_q, the root-mean-square height (based on ISO 25178-2), was calculated as follows:

$$S_q = \sqrt{\frac{1}{A}\iint_A z^2(x,y)dxdy}\,. \quad (1)$$

Here, A denotes the definition area of the image.

2.5 | Water uptake

To examine the influence of the wet storage condition on the PU materials, water uptake tests were conducted for a time span of 50 days. Therefore, the samples (~1 mm^2) were first dried in a ventilated oven at 40°C for 4 days. Afterward, the initial mass of each sample was determined using a microscale (XSE205 DualRange; Mettler Toledo). Then, the samples were immersed into 1 ml of DPBS and incubated at 37°C while avoiding liquid evaporation. At various time steps, samples were removed from the incubation bath, their surface was dried with a laboratory wipe, and they were weighed again to determine the relative change in mass.

2.6 | UV treatment

For treatment with ultraviolet light, samples were placed in a commercial UV sterilization chamber (BLX-254; Vilber-Lourmat GmbH), working at a wavelength of 254 nm (4 × 8 W), and exposed to UV light for 10 and 30 min, respectively. In Rickert et al.,[22] it was shown that 10 min of direct exposure to UV generated by the very same device is sufficient to disinfect materials. However, here, immersed samples stored in buffer should also be disinfected; thus, the exposure time had to be increased to 30 min to ensure that a sufficient UV intensity reached the surface of the PU samples. To decide if any surface differences detected after UV irradiation were specific to the surface treatment applied before UV exposure or rather material-dependent alterations, both untreated (= control group) and treated (= plasma-treated or dopamine-treated) PU samples were exposed to UV light.

2.7 | In vitro tests with eukaryotic cells

2.7.1 | Cell cultivation

Human epithelial cells (HeLa) were cultured in Minimum Essential Medium Eagle (Sigma-Aldrich) containing 10% (v/v) fetal bovine serum (Sigma-Aldrich), 2 mM L-glutamine solution (Sigma-Aldrich), 1% non-essential amino acid solution (Sigma-Aldrich), and 1% penicillin/streptomycin (Sigma-Aldrich). Incubation was conducted in a humidified environment at 37°C with 5% CO_2.

2.7.2 | Biocompatibility test

Biocompatibility of the different PU sample surfaces was investigated using a water-soluble tetrazolium (WST-1) assay (Sigma-Aldrich). For this purpose, wells of a 96-well plate were filled with two medical-grade PU materials (AC and PC; at least three replicates for each material/surface modification combination). The sample-containing wells were then washed three times with sterile DPBS. Afterward, each sample was incubated with 30 000 cells for 24 h. After this incubation step, all samples were washed with sterile DPBS and, in each well, the buffer was replaced with 200 µl of media supplemented with a 2% (v/v) WST-1 solution. The cells were incubated for 1 h and, after transferring 100 µl from each well into a new plate, the absorption behavior of the solutions was quantified at an excitation wavelength of 450 nm (Varioskan LUX; Thermo Fisher Scientific). In addition, images of the treated cells were recorded on an inverted light microscope (DMi8 Leica; Leica) using phase-contrast settings, a ×10 lens (Leica, A-Plan, ×10/0.25 Ph1), and a digital camera (Orca Flash 4.0 C11440; Hamamatsu).

2.8 | Tribology

2.8.1 | Sample preparation

PUR samples were prepared as rectangular samples with a size of 5 × 12 mm; in this shape, they could be used directly in a ball-on-three-plates geometry making use of a commercial sample holder (Anton Paar). Before the

friction measurements, a subset of the prepared samples was plasma treated (as described above) and another subset was dopamine treated (as described above). To ensure a comparable hydration of the different PU variants, untreated and plasma-treated samples were additionally immersed into ddH_2O for 3 h (this is the same incubation time as that used during the dopamine treatment step).

2.8.2 | Friction measurements

For friction measurements, a commercial shear rheometer (MCR 302; Anton Paar) was equipped with a tribology unit (T-PTD 200; Anton Paar). As a counterpart, steel spheres with a diameter of 12.7 mm (1.4301, $S_q < 0.2\,\mu m$; Kugel Pompel) were used. Three PUR samples were mounted onto the sample holder and covered with 600 µl of 20 mM HEPES buffer (pH 7) as an aqueous lubricant. All tests were performed at a constant temperature of 21°C, and in each test, the sliding velocity was varied from 1000 to 0.1 mm s^{-1}. Measurements were conducted at a constant normal load of $F_N = 6$ N. This normal force was chosen such that, within the accessible speed range, friction in the boundary, mixed, and hydrodynamic regimes could be probed. Based on the Hertzian contact theory,[23] the average contact pressure p_0 was estimated as follows:

$$p_0 = \frac{2}{3}p_{max} = \frac{2}{3\pi}\sqrt[3]{\frac{6 \times F_{N,per\ pin} \times E'^2}{R_{sphere}^2}} \quad \text{with} \quad \frac{1}{E'} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}. \tag{2}$$

For steel, Young's modulus of $E_{steel} = 210$ GPa and a Poisson's ratio of $\nu_{steel} \approx 0.3$ were used. However, for PUR, the manufacturer lists neither of those material parameters in the material specification sheets; only the Shore A hardness ($Sh_A = 72$ A) is given. Thus, Young's modulus of PUR was estimated by combining the theory of Boussinesq[24] (which connects the indentation depth into a material with its Young's modulus) with linear correlations derived from the specifications given in the normed protocols to determine the Shore A hardness. Using this approach, the following estimation was obtained:

$$E_{est.} = \frac{1-\mu^2}{2R_{probe}C_1} \times \frac{C_1 + C_2 \times Sh_A}{100 - Sh_A}. \tag{3}$$

Here, $R_{probe} = 0.395$ mm is the radius of the indentation probe used in the hardness test and $C_1 = 0.549$ N, $C_2 = 0.07516$ N, and $C_3 = 0.025$ mm are constants derived from physical specifications of the Shore A hardness test.[25] With these values, an estimated Young's modulus of $\sim E_{PUR} = 8.6$ MPa was obtained. Furthermore, a Poisson's ratio of $\nu_{PU} = 0.45$ was assumed, as $0.4 \leq \nu \leq 0.5$ is typical for flexible (rubber-like) polymers such as elastomeric PUs.[26] Together, this results in an estimated average contact pressure of $p_0 = 0.77$ MPa and a contact area of $a = 0.88$ mm^2.

2.8.3 | Statistical analysis

Tests for statistical significance were conducted for all quantitative results shown in Figures 1 and 3 as well as for biocompatibility tests shown in Figure 4. Each set of samples was first tested for a normal data distribution using a Lilliefors test; then, a two-sample F test was applied to check for equal variances. To test for significant differences between normally distributed samples, a two-sample t test was applied when homogeneity of variances was confirmed, whereas a Welch's t test was performed for heteroskedastic sets of samples. For samples that were not normally distributed, a Wilcoxon–Mann–Whitney test was performed. All statistical analyses were conducted using Microsoft® Excel® for Microsoft 365 (Version 2108; Microsoft Corporation) with add-in Real Statistics Resource Pack software (Release 7.6, Copyright 2013–2021; Charles Zaiontz); differences were considered statistically significant if a p value below 0.05 was obtained.

3 | RESULTS AND DISCUSSION

In a first step, the influences of different treatment strategies on the surface properties of three PU variants are examined. These PU variants comprise a technical polyurethane (PUR) and two medical-grade PUs (PC, AC—see Section 2). The aim of this first set of experiments is to test which of the three surface treatment strategies improves the wetting behavior of the polymeric material without inducing macroscopic or microscopic alterations to the surface properties of the PU materials. With initial CAs of 99.8 ± 0.65° and 93.9 ± 0.62°, the wetting properties of untreated PC and PUR, respectively, are located right in the transition zone between hydrophobic (CA > 90°) and hydrophilic (CA < 90°) behavior (Figure 1a,b); in contrast, untreated AC samples already show slightly hydrophilic behavior as indicated by CA values of 76.1 ± 0.78° (Figure 1c). Thus, a particular surface treatment is considered successful if those CAs are

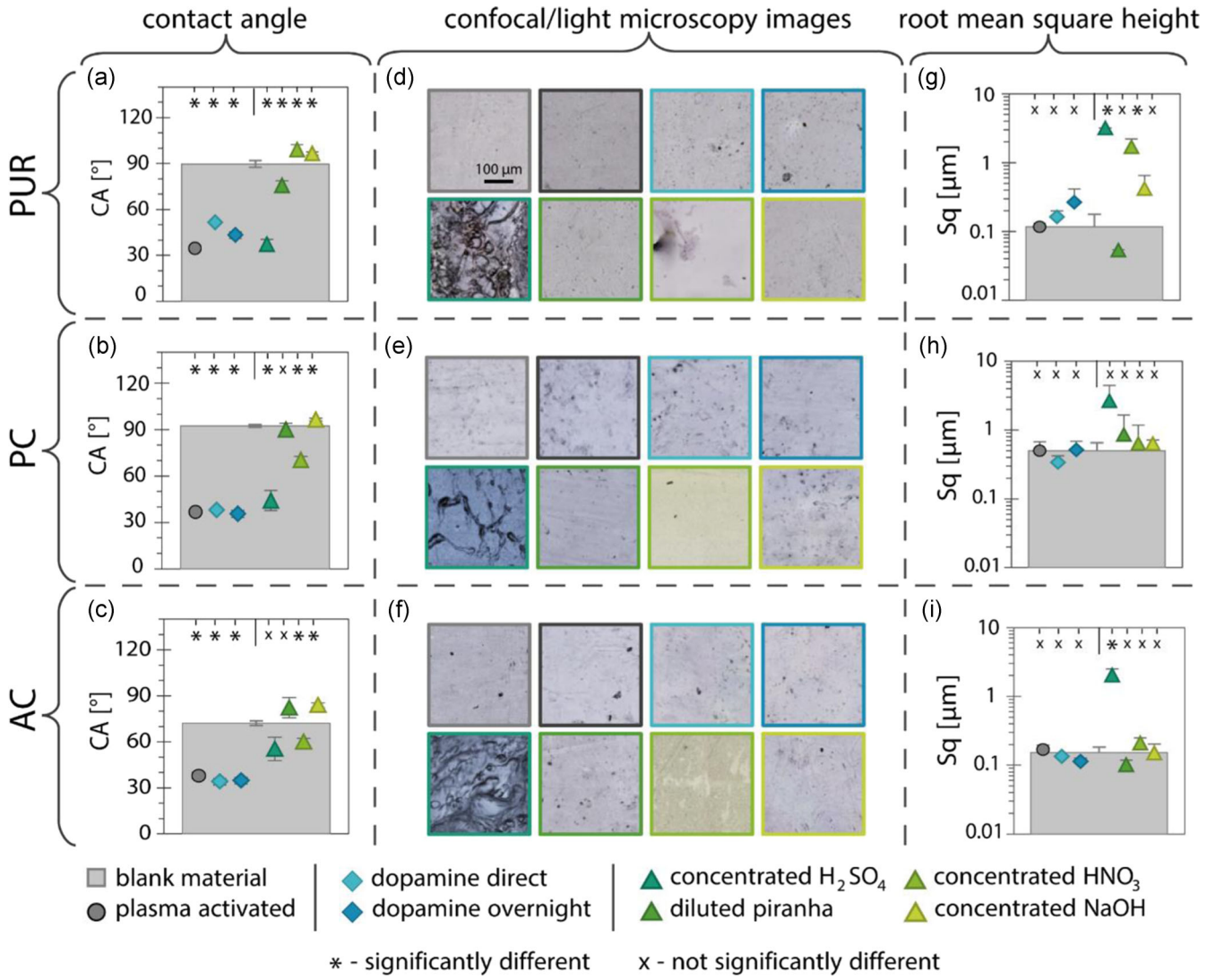


FIGURE 1 Influence of different treatment strategies on the surface properties of polyurethane materials: (a–c) the results of water contact angle measurements; (d–f) combined laser confocal and light microscopy images acquired at a ×50 magnification; and (g–i) quantification of the samples' surface roughness via the root-mean-square height S_q. Each aspect was assessed for three different polyurethane materials: (a, d, g), PUR; (b, e, h), PC; and (c, f, i), AC. Data were obtained before (light gray bars) and after the implementation of the designated surface activation strategies (other colors/symbols). The tested surface treatment strategies include plasma activation (dark gray/circles), two types of dopamine treatments (light blue and dark blue/diamonds), and four chemical etching approaches (different shades of green/triangles). The scale bar in (b) represents 100 µm and applies to all microscopy images in (d–f). Error bars denote the standard error of the mean as obtained from at least $n = 3$ measurements. If no error bars are visible, their size is on the order of the symbol size. Results determined to be significantly different from those obtained for the corresponding blank material sample are marked with an asterisk (based on a p value of 0.05); otherwise, the results are marked with a cross. AC, aromatic Carbothane™ AC-4095A; PC, aliphatic Carbothane™ PC-3575A; PUR, elastomeric polyurethane THOMAPLAST®-PUR

reduced to ~45° or below; such a result would represent a clearly hydrophilic wetting behavior. Indeed, both plasma treatment and dopamine treatment achieve this goal for all three PU variants. In contrast, the chemical etching strategies are less efficient as we only obtain satisfactory results with concentrated sulfuric acid (H_2SO_4).

However, as mentioned above, it is important that an improvement in the wetting properties does not arise at a too high price: Examples of undesired side effects that one of the surface treatment strategies could induce include noticeable color changes in the material or strong topographical alterations. To test for these alterations, the treated PU variants are next investigated under a confocal laser scanning microscope.

Combined confocal/light microscopy images (Figure 1d–f) clearly show that, for all three materials, a treatment with concentrated sulfuric acid leads to drastic

alterations of the sample surface: here, different from the even and homogeneous appearance of the untreated materials, major structural changes are visible. This qualitative impression is underscored when the surface roughness parameter S_q (i.e., the root-mean-square height) is calculated (Figure 1g–i) from the topographical information provided by the profilometric images: This metrological analysis shows that neither plasma treatment nor the two dopamine treatments lead to a significant alteration in the surface roughness. In contrast, exposure to sulfuric acid increases the roughness of all three PU variants. In other words, all etching solutions tested here either fail to sufficiently decrease the CA of the PU materials (piranha solution, NaOH) or induce obvious surface alterations (i.e., topographical changes in the case of H_2SO_4 and color alterations in the case of HNO_3). Thus, in the rest of this article, chemical etching of the different PU materials is not considered further.

For many applications, in addition to being efficient, it is equally important that a surface treatment entails changes in the material properties that are stable over an extended time period. Thus, in a next step, we investigate the durability of the hydrophilizing effect achieved by the different surface treatments. In detail, two storage conditions are examined: first, wet incubation at body temperature (i.e., samples immersed in DPBS and stored at 37°C) and second, dry incubation in the cold (i.e., storage at 4°C without any added buffer). Here, the first scenario mimics conditions that the PU variants will encounter in or on the human body, for example, when used as materials for implants or medical devices; in contrast, the second set of storage parameters can be relevant for medical products before their application in vivo or for PU-based materials that are used outside a living organism.

As control groups, untreated samples are immersed into a buffered solution and stored at 37°C. For those untreated samples, such wet storage gives rise to a slight decrease in the CA. This effect takes place within the first 5 days of storage and is the mildest for AC and the strongest for PUR; after this time point, the CA values stabilize and remain constant for the rest of the observation period (see Figure 2a–c). A similar trend is observed when the water uptake behavior of these samples is quantified: we find the strongest effect for PUR (where we measure an increase of ~2% [w/w]) and weaker changes (i.e., a weight increase ~1% [w/w]) for AC and PC (Figure 2d). This suggests that these two phenomena, water uptake and a decrease in the CA upon storage in aqueous solutions, are related.

Overall, when comparing wet and dry storage of treated samples, the former seems to be preferable for all three PU variants and for all treatment strategies tested; here, the CA values stabilize at much smaller numbers than under dry storage conditions (Figure 2e–g). This suggests that using the treated samples in an application where they are continuously exposed to an aqueous environment would be ideal. For dopamine-treated PU samples stored under wet conditions, we measure CA values as low as 20–30°, and these are stable for at least 2 weeks. Plasma-treated samples slightly recover over time and stabilize at somewhat larger CAs between 40° and 50°; however, also, these values correspond to clearly hydrophilic behavior. When stored under wet conditions, we find the best durability of all surface treatments for AC samples (Figure 2c): here, after the 4th day, we detect virtually no change in the measured CA values anymore.

In contrast, when stored under dry conditions, all surface-treated PU variants lose, to a certain extent, their initially strong hydrophilic properties over time. Such a behavior is known as "hydrophobic recovery" and resembles previous results obtained with other polymeric materials such as polydimethylsiloxane (PDMS),[27–30] polypropylene,[31–33] polyethylene,[34] and polytetrafluorethylene.[35,36] For most of these materials (when stored in air), this hydrophobic recovery occurs within the first 2–7 days.[28,30,31,36] In these publications, this effect was mainly attributed to a migration of the polar groups created by the plasma treatment from the surface of the material into the sub-surficial polymeric volume, for example, via diffusive motion of polymer chains or by reorientation/rotation of polymer segments carrying the hydrophilic residues.[37] Also, for those other polymeric materials, this process of hydrophobic recovery slowed down when the samples were stored in a polar medium (e.g., phosphate-buffered saline); there, this was attributed to stabilizing effects arising from interactions between the surface-bound polar (hydroxyl) groups created by plasma treatment and the polar solvent covering the surface.[27,28,35,36]

Of course, in addition to the storage conditions (including storage time, temperature, and the surrounding medium),[28,31,35] hydrophobic recovery can also be influenced by certain treatment parameters such as the plasma type[13,38] and the technical settings used during the plasma treatment[32,36] as well as the specific properties (e.g., the degree of crystallinity[32,33] and the glass transition temperature[39]) of the treated material. Thus, it is not surprising that the kinetics of hydrophobic recovery is slightly different for all three PU variants examined here. For plasma-treated AC samples, hydrophobic recovery is the strongest; in contrast, for PUR samples, we still observed a considerably reduced CA at the end of the stability test.

Even though dry storage of all treated samples leads to a clear increase in the CA within the first few days (all

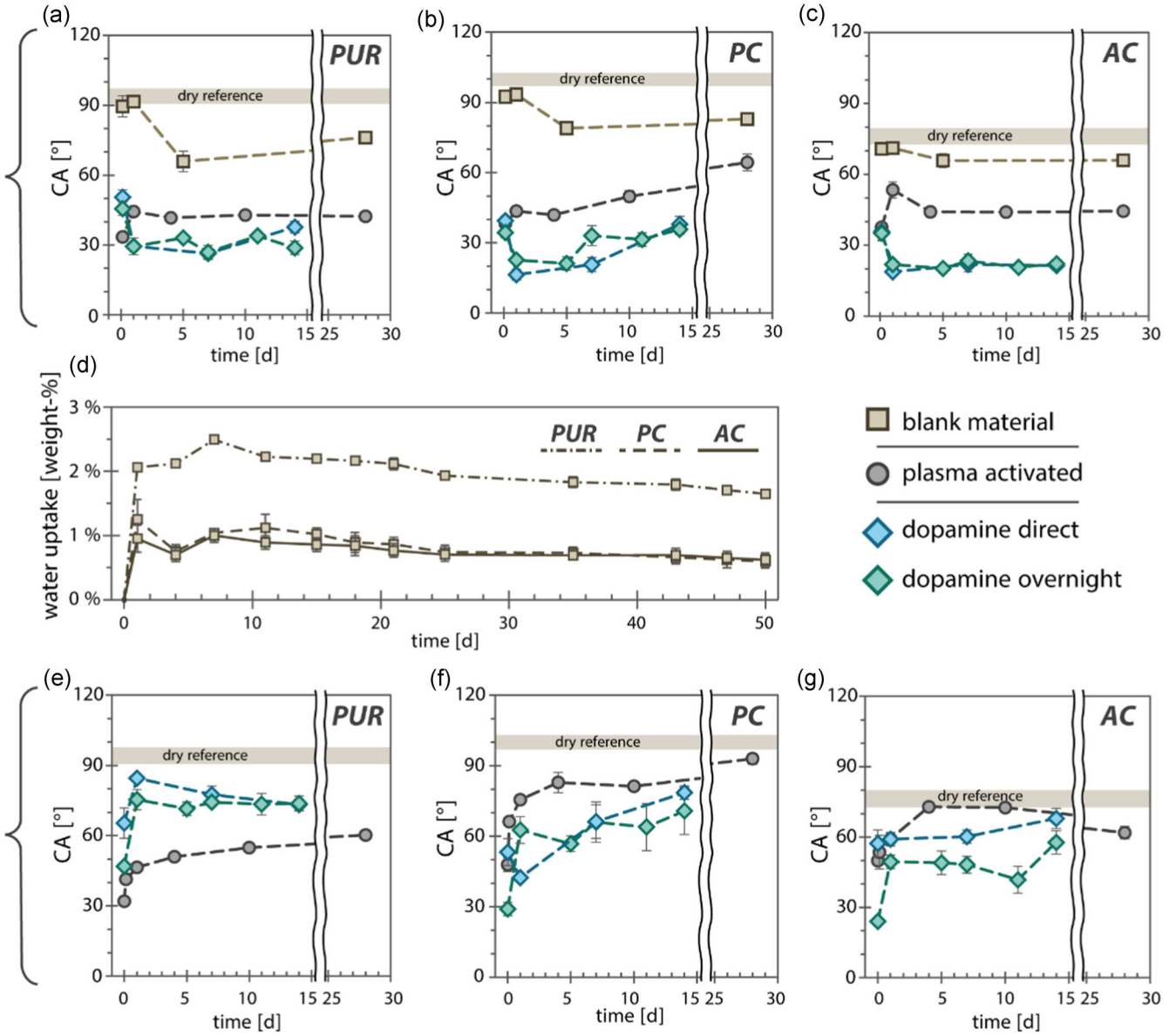


FIGURE 2 Durability of different surface modifications of PU materials during sample storage: Contact angle measurements conducted over a period of 2–4 weeks are shown for untreated/blank (beige squares), plasma-activated (gray circles), "dopamine-direct"- and "dopamine-overnight"-treated (blue/turquoise diamonds) samples. Samples were either stored in the wet state (i.e., in physiological buffer at 37°C; a–d) or in the dry state (at 4°C; e–g). For wet storage, the data shown in (d) describe the water uptake behavior of the PU samples as determined by the relative change in weight. Error bars denote the standard error of the mean as obtained from at least $n = 3$ measurements. If no error bars are visible, their size is on the order of the symbol size. AC, aromatic Carbothane™ AC-4095A; PC, aliphatic Carbothane™ PC-3575A; PU, polyurethane; PUR, elastomeric polyurethane THOMAPLAST®-PUR

CA values are above 45° after 5 days of dry storage), it is worth noting that the "dopamine overnight"-treated AC samples, all treated PC samples, and all treated PUR samples maintain improved wetting properties (i.e., at least 15–20° difference) and did not fully recover their initial CA values for at least 2 weeks. Plasma-treated PUR samples performed the best: here, even after a month of storage, the measured CA values were still lower by ~50° than those determined for untreated samples.

As no clear difference between the outcomes of dopamine-overnight- and dopamine-direct-treated samples in any of the previous tests could be observed, for practical reasons, the following tests are only performed with one type of dopamine treatment. Thus, for the rest of this article, the dopamine-direct treatment of the different PU materials is not considered further.

For many applications, a germ-free material surface is required. However, as the conditions of an autoclave

treatment (high temperature + high humidity + high pressure) are expected to adversely affect the shape and structure of the samples (due to, e.g., softening, hydrolysis, and pyrolysis), milder disinfection methods are needed to reduce potential microbial contamination of the materials. Here, we use UV irradiation as a possible disinfection method and investigate the influence of such UV exposure on the material properties of the three PU variants and the different hydrophilizing surface treatments applied to them. As described above, the wettability of the differently treated surfaces (as quantified by the CA) is a good indicator of successful surface modification. Thus, we again use CA measurements to evaluate the influence of UV exposure on the surface properties of the different activated PU variants.

First, blank (= not surface modified) samples are tested to assess the putative effects that a UV exposure might have on the base materials themselves. Yet, we detect only minor differences between the wetting properties of untreated and UV-treated samples (Figure 3), independent of whether the UV exposure occurred in a "wet state" or a "dry state." Consequently, all obvious changes in the CA of surface-treated samples that we might detect later are likely to originate from alterations in the surface activations as induced by the UV exposure. Interestingly, we find that UV irradiation only affects selected conditions: For plasma-treated samples, hydrophobic recovery seems to be accelerated by a UV treatment conducted in the dry state. This effect is the weakest on PUR, which is in line with our findings described above (see Figure 2e), where plasma-treated PUR samples were most stable when stored in the dry state. The plasma-treated PUR samples in the wet state are the only plasma-treated samples that do not show any changes for either of the exposure times.

In contrast, for dopamine-treated AC and PC samples in a wet state, UV exposure of samples even significantly decreases the CA values. As dopamine is reported to be UV sensitive,[40] we speculate that this effect might be due to further stabilization of the wet dopamine layer by the UV light. However, in the dry state, the UV irradiation once more seems to have negative effects on the dopamine-treated surfaces.

Having shown that most hydrophilized PU samples can be subjected to a UV treatment without compromising the surface activation effect, we next investigate the interaction of the PU materials with eukaryotic cells. For this subset of tests, we focus on AC and PC, as these two materials (in contrast to PUR) have been developed for medical use. As a model cell line to conduct colonization and cytotoxicity tests with, we select the well-established epithelial cell line HeLa.[16,41] Such HeLa

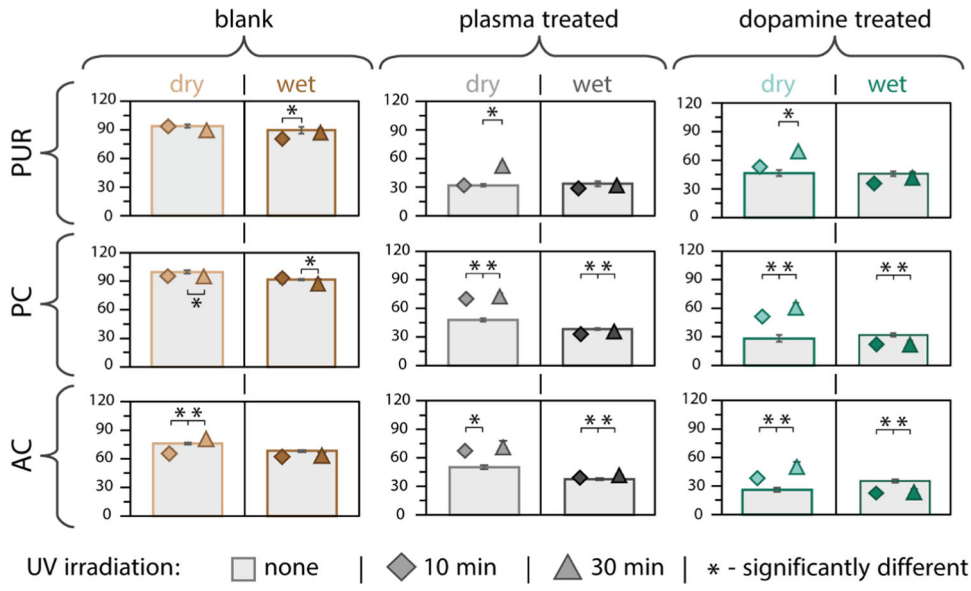


FIGURE 3 Influence of UV irradiation on the surface wettability of different PU samples: Contact angles were determined on all three materials before UV irradiation (gray bars), and after 10 min (diamonds) and 30 min (triangles) of UV exposure. Results are shown for untreated (blank, left column), plasma-treated (middle column), and "dopamine overnight"-treated (right column) samples. The samples were either exposed to UV light in a "dry state" (light colors) or a "wet state," that is, when covered by a water layer of ~1 cm thickness (dark colors). Error bars denote the standard error of the mean as obtained from at least $n = 3$ measurements. If no error bars are visible, their size is on the order of the symbol size obtained from at least $n = 3$ measurements. Results determined to be significantly different from those obtained for the corresponding blank material sample are marked with an asterisk (based on a p value of 0.05). AC, aromatic Carbothane™ AC-4095A; PC, aliphatic Carbothane™ PC-3575A; PU, polyurethane; PUR, elastomeric polyurethane THOMAPLAST®-PUR

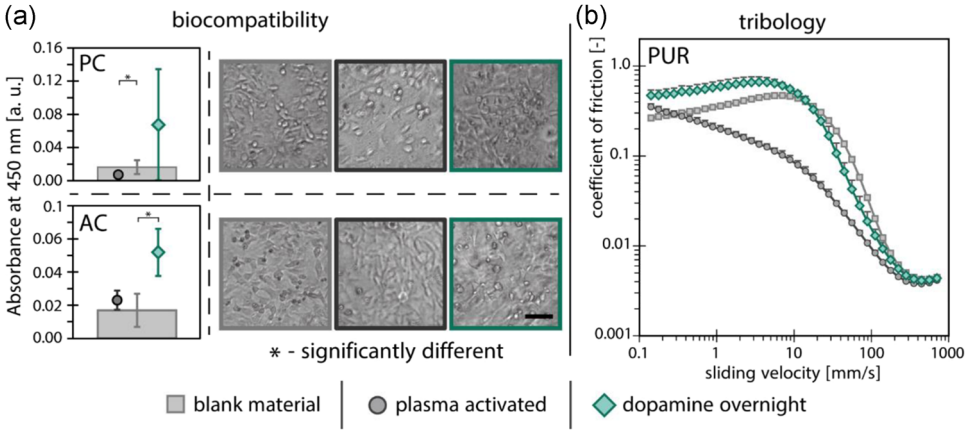


FIGURE 4 Functional examination of surface-treated PU variants. (a) To assess the biomedical functionality of PC and AC, the viability of HeLa cells seeded onto the PU materials is determined using a WST-1 test (left), and phase-contrast images show the morphology of adherent cells (right). The scale bar corresponds to 50 μm and applies to all microscopy images in this subfigure. The error bars denote the standard deviation as obtained from six independent samples obtained from at least $n = 3$ measurements. If no error bars are visible, their size is on the order of the symbol size. Results determined to be significantly different from those obtained from the corresponding blank material sample are marked with an asterisk (based on a p value of 0.05). (b) A technical application of PUR samples is tested via a tribological examination of (un)treated PUR samples in a rotational ball-on-three-plates setup. Error bars denote the standard error of the mean as determined from at least $n = 3$ sample sets. If no error bars are visible, their size is on the order of the symbol size. AC, aromatic Carbothane™ AC-4095A; PC, aliphatic Carbothane™ PC-3575A; PU, polyurethane; PUR, elastomeric polyurethane THOMAPLAST®-PUR

cells are seeded onto the two PU variants to investigate the morphology and metabolic activity of those cells when colonizing AC and PC surfaces, respectively (Figure 4a, left).

On both untreated AC and PC material surfaces, we find good surface coverage with HeLa cells, and the well-spread asymmetric morphology of these cells is consistent with what one would expect for viable epithelial cells seeded onto a stiff substrate (Figure 4a, right). This result is in line with statements of the manufacturer that Carbothanes are biocompatible, medical-grade PUs.[42]

Whereas plasma activation of the two PU materials hardly entails any alterations with regard to cell colonization, dopamine treatment improves this material property. This is demonstrated by a higher cell density that we find on the dopamine-treated samples that is accompanied by a stronger signal obtained from a WST-1 test: On the dopamine-treated surfaces, the metabolic activity reported by the absorbance signals is ~2 (AC) or ~3 times (PC) as high as that for unmodified AC and PC samples, respectively. This result is in agreement with similar tests conducted with other synthetic materials coated with dopamine[43,44] and demonstrates that this surface treatment strategy can promote cell colonization while avoiding cytotoxic effects.

Finally, for the PUR samples, which are not used in a medical context, we also assess a material property that is relevant for an important application area; as PUR samples are used in many technical settings, here, we chose a rotational tribology test to examine the influence of the different surface treatments on the friction behavior of PUR. Compared to untreated PUR, we observe that dopamine treatment mostly maintains the friction response of the sample; only in the boundary lubrication regime do we detect a slightly increased friction factor (Figure 4b). Even though one might have assumed that an improved interaction with the lubricant as brought about by the dopamine treatment could lead to reduced friction, this finding agrees with previous results from the literature: dopamine forms an adhesive layer to which other objects readily stick. Whereas this property is beneficial for attaching other molecules to the dopamine layer,[45] here, it counteracts the improved interaction of the surface with aqueous solutions by restricting the sliding motion of the steel sphere, thus resulting in increased coefficients of friction, yet only at slow sliding speeds. This result can be explained by the Stribeck theory[46]: as stated there, with increasing relative sliding velocities, the contact of the two surfaces in a tribological material pairing is reduced as a thin lubricating liquid layer is formed in between the surfaces. Accordingly, the stickiness of a surface becomes less relevant when moving from the boundary lubrication regime into the mixed (or even hydrodynamic) lubrication regime, as the contact of the steel sphere with the adhesive layer is reduced. In full agreement with this picture, we find that plasma-treated samples (which show enhanced wettability, but have non-sticky surfaces) show

a reduced friction response in both the mixed and most of the boundary lubrication regime, and this can be attributed to improved interactions of the hydrophilized surface with the aqueous lubricant. As a consequence of the improved surface wetting behavior, one or more of the following two effects can occur: first, as the plasma treatment leads to a more polar surface, the (polar) water molecules have more possibilities (with higher degrees of freedom) to interact with the material surface. Second, a thin hydration layer can be generated on the surface of the PUR, which might promote separation of the two tribological partners even at slower sliding velocities. Thus, at intermediate sliding speeds of ~10 mm s^{-1}, the resulting friction reduction is approximately on the order of a factor of 5, which is high for a high-friction material such as PUR.

4 | CONCLUSIONS

In summary, here, we have shown that oxygen plasma treatment and dopamine deposition are two highly suitable surface treatment strategies to enhance the wettability of different PU materials. With either method, we observed good stability of the achieved surface modification for at least 2 weeks, and these modifications are robust toward UV irradiation (when applied to samples stored in the wet state) as required for sample disinfection. In terms of certain aspects, the dopamine treatment appeared somewhat superior to the plasma treatment; nevertheless, the best treatment option depends on the specific material as well as the intended application. Also, for each application/material combination, optimization of the process parameters used for the surface modification process could further improve the properties of the differently treated PU variants. An interesting advantage provided by the dopamine-based strategy could be that it allows for an easy attachment of a macromolecular top layer to enable hydration lubrication (thus reducing friction) or to initiate multistep coatings as useful for drug storage/release approaches.[47] Similarly, also, the plasma treatment can serve as an initial step for further surface functionalization, for example, when followed by silanization and subsequent carbodiimide-mediated coupling of a macromolecular layer.[48] Indeed, both approaches have previously been used to reduce friction and wear generation[44,48,49] and to reduce the adsorption of proteins, cells, and bacteria[18,44]; however, to date, such multifunctional coatings have been mainly applied to other polymeric materials such as PDMS or polytetrafluorethylene. Existing coatings of PU materials, in contrast, often aim at merely individual characteristics, *e.g.*,hemocompatibility or antibacterial properties of the material.[50] Certainly, PU materials would benefit from more complex, multifunctional coatings, and the corresponding additional properties (in particular, an improved friction behavior) brought about by their use would further increase the range of applications that they can be used for.

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CONFLICT OF INTERESTS

The authors declare that there are no conflict of interests.

AUTHOR CONTRIBUTIONS

This study was conceptualized by Maria Bauer and Oliver Lieleg; Rosa Reithmeir contributed to contact angle measurements; Theresa Lutz performed experiments involving eukaryotic cells; and Maria Bauer performed all other experiments and analyzed the data. The manuscript was written by Maria Bauer and Oliver Lieleg and was critically revised by all authors.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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