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Fluorination of poly(dimethylsiloxane) surfaces by low pressure CF_4 plasma – physicochemical and antifouling properties

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Abstract. Fluorinated surface groups were introduced into poly(dimethylsiloxane) (PDMS) coatings by plasma treatment using a low pressure radio frequency discharge operated with tetrafluoromethane. Substrates were placed in a remote position downstream the discharge. Discharge power and treatment time were tuned to alter the chemical composition of the plasma treated PDMS surface. The physicochemical properties and stability of the fluorine containing PDMS were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and contact angle measurements. Smooth PDMS coatings with a fluorine content up to 47% were attainable. The CF_4 plasma treatment generated a harder, non-brittle layer at the top-most surface of the PDMS. No changes of surface morphology were observed upon one week incubation in aqueous media. Surprisingly, the PDMS surface was more hydrophilic after the introduction of fluorine. This may be explained by an increased exposure of oxygen containing moieties towards the surface upon re-orientation of fluorinated groups towards the bulk, and/or be a consequence of oxidation effects associated with the plasma treatment. Experiments with strains of marine bacteria with different surface energies, *Cobetia marina* and *Marinobacter hydrocarbonoclasticus*, showed a significant decrease of bacteria attachment upon fluorination of the PDMS surface. Altogether, the CF_4 plasma treatments successfully introduced fluorinated groups into the PDMS, being a robust and versatile surface modification technology that may find application where a minimization of bacterial adhesion is required.

Keywords: *coatings, plasma treatment, poly(dimethylsiloxane), fluorination, marine bacteria*

1. Introduction

Low pressure plasma based processes are a versatile tool for surface modification of polymers. Depending on the plasma parameters, plasma etching or material deposition can predominate [1]. In the intermediate case, a surface layer with a thickness of few tens of nanometers is modified [2]. This type of plasma treatment is relevant for a wide variety of applications. With a simple one-step procedure the surface properties of the polymer can be changed significantly while the bulk properties remain unchanged. On the other hand, there are well-known drawbacks of this technique, as the heterogeneity of the obtained surface chemistry [3] and the lack of longterm stability (hydrophobic recovery) [4]. However, low pressure plasma treatment of polymers is an attractive approach, at least from a technological point of view, and many strategies were proposed to avoid or minimize the unfavourable mentioned side-effects. These

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include the covalent grafting of appropriate molecules onto plasma activated surfaces or the durable adsorption of polyelectrolytes on charged surfaces (as obtained for example after ammonia plasma treatment) [5]. In addition to modification of surface chemical composition, plasma techniques have also been used to modify the surface morphology (roughening) of polymeric surfaces aiming for example at changes in wetting behaviour [6–8].

Poly(dimethylsiloxane) (PDMS) is a commercially available type of silicone rubber widely used in the fabrication of medical [9] and microfluidic devices [10], and as foul-release coating to control marine biofouling [11, 12]. Foul-release coatings are currently a successful non-toxic, environmentally friendly alternative to classical biocide-containing coatings [12]. Commercially available foul-release coatings are based on silicone elastomers since these possess a combination of properties that minimize the chemical and mechanical locking of the fouling species [13].

In this paper we report on the fluorination of PDMS (Sylgard 184) by application of tetrafluoromethane (CF_4) plasma to combine the bulk elasticity of PDMS with a desirable surface chemistry, without introducing changes in surface roughness. Towards this goal, a customized low pressure plasma set-up with a sample position far away from the excitation volume of the discharge was used to fabricate surfaces with a particularly high fluorine content consisting mainly of CF_2 and CF_3 moieties. This approach based on remote plasma configuration ensures an especially smooth but efficient treatment. The properties and stability of the fluorine containing PDMS were characterized in detail concerning chemical composition by X-ray photoelectron spectroscopy (XPS), morphology and elasticity by atomic force microscopy (AFM) and wetting by contact angle measurements. The antifouling potentialities of the CF_4 plasma treated PDMS towards microbes were evaluated by testing the attachment and adhesion strength of two species of bacteria (*Marinobacter hydrocarbonoclasticus* and *Cobetia marina*). These bacteria form biofilms that coat surfaces when in contact with sea water – either when surfaces are immersed in the sea (e.g. ship hulls) or are exposed to sea water (as in cooling systems) [14].

2. Experimental

2.1. Materials

The silicone elastomer Sylgard 184 and the Primer 1200 OS were purchased from Dow Corning (Germany). Tetrafluoromethane (99.99%) was obtained from Messer Griesheim (Germany). For stability tests and surface characterization experiments an artificial sea water (ASW*) solution was prepared using the five main components of natural sea water as described in ASTM D 1141–98 (24.53 g/l NaCl; 5.20 g/l $MgCl_2$; 4.09 g/l Na_2SO_4; 0.695 g/l KCl; 1.16 g/l $CaCl_2$) [15]. The ASW* solution was prepared using high purity salts and autoclaved before use. For the assays with marine bacteria, SSP growth medium (containing sea salt and peptone) was purchased from Sigma Aldrich (Germany), and natural sea water (SW) was collected in Den Helder, The Netherlands.

2.2. Sample preparation

Poly(dimethylsiloxane) (PDMS) coatings were prepared on inorganic carriers of variable dimensions for further modification by low pressure CF_4 plasma treatment. The PDMS coatings were fabricated using the two-part elastomer Sylgard 184. The elastomer was prepared using a ratio base to curing agent 10:1 (weight), following the suggestion of the manufacturer. The base and curing agent were mixed using a homogeneizer (Kontes; USA) for 3 min and then degassed under vacuum until all air bubbles were removed (ca. 30 min). The polymer was then deposited onto either silicon wafers of different sizes for physicochemical analysis, or onto standard microscope glass slides (26×76 mm^2) for biological testing.

Silicon wafers were coated by pouring defined amounts of pre-polymer (depending on the wafer dimensions) onto the cleaned surface. The pre-polymer was air-spread for complete, homogeneous coverage of the surface. The coatings were cured at 65°C for 5 h 45 min.

For preparation of PDMS coatings onto standard microscopy slides used to test bacteria biofilm formation and release, an *in-house* film preparation system was developed (Figure 1). This consists of a metallic base onto which the glass slides were

Figure 1. *In-house* developed setup for preparation of homogeneous PDMS coatings with defined thickness onto standard microscope slides

assembled using an adhesive foil. Since the bacterial adhesion strength tests implied exposing the coatings to high shear, there was a need to improve adhesion between PDMS and glass to avoid failure during testing. This was achieved by applying a thin layer of the adhesion promoter Primer 1200 OS onto the clean glass surface. After assembly of the cleaned slides into the film preparation system, a thin layer of the adhesion promoter was applied onto the glass surface by using a fiber-free tissue (following the instructions of the provider). After 30 min, Sylgard 184 was poured onto the immobilized microscope slides and spread until homogeneous coverage of the surface. PDMS coatings with desired, well-defined thickness were then obtained using the film applicator. The metallic base containing the immobilized samples was incubated at 65°C for 45 min, after which the samples were removed from the metallic holder and further cured at 65°C for 5 h.

2.3. MicroGlider®

The topography and thickness of the PDMS coatings prepared onto standard microscope slides was examined using a MicroGlider (Fries Research & Technology GmbH, Germany). The MicroGlider operates on the principle of chromatic aberration. It functions as an optical profilometer (2D) and as an imaging measuring instrument (3D) by means of a scanning process. The MicroGlider was applied for the evaluation of surface morphology and thickness of the PDMS coatings because of its large-scale vertical resolution (from 10 nm to 300 μm), and the possibility to investigate large sample areas (up to 100×100 mm^2). The lateral resolution is, however, determined by the spot size of the reflected light on the sample and is about 1–2 μm.

2.4. Plasma treatment

The low pressure plasma set-up is shown schematically in Figure 2. The vacuum system consists of a quartz tube with an inner diameter of 20 mm and a length of 300 mm on top of a cylindrical part with an inner diameter of 200 mm and a length of 800 mm connected to a rotary vane pump. Tetrafluoromethane (CF_4) is introduced into the chamber by a gas flow control system. Pressure is measured by a capacitive vacuum gauge. The control unit is connected to a butterfly valve between the pump and the chamber and allows to set a particular pressure for a given gas flow. For plasma generation electrodes are attached to the outer surface of the quartz tube. The electrodes are connected to a 13.56 MHz radio frequency (RF) generator (Hüttinger PFG300RF) via an automatic matching network. This leads to a discharge operated in the small diameter tube. The distance between the discharge and the electrically grounded sample holder in the bottom part of the chamber was set to 60 cm.

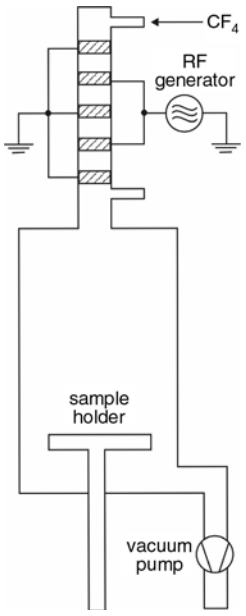

Figure 2. Low pressure plasma set-up

For the investigations of this work the set-up was operated with a CF_4 flow of 42 standard cm^3/min and a pressure of $7 \cdot 10^{-2}$ mbar. Distinct parameter sets regarding the effective RF power and the treatment time were applied.

2.5. X-ray photoelectron spectroscopy

XPS was carried out using an Amicus spectrometer (Kratos Analytical, UK) equipped with a non-monochromatic Mg K_α X-ray source operated at 240 W and 8 kV. The kinetic energy of the photoelectrons was determined using an analyzer with a pass energy of 75 eV. The take-off angle between the sample surfaces's normal and the electron optical axis of the spectrometer was 0°. In this case, the information depth is about 8 nm. Spectra were referenced to the 1s peak of aliphatic carbon at 285 eV. A satellite subtraction procedure was applied. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. High-resolution spectra were deconvoluted by means of CasaXPS (Casa Software Ltd., UK).

2.6. Atomic force microscopy

Morphological features of the PDMS surface before and after CF_4 plasma treatment were characterized by atomic force microscopy (AFM) in tapping mode (Nanoscope IIIa Dimension 3100, Veeco, USA) using silicon cantilevers (Budget Sensors, Bulgaria) with a tip radius lower than 10 nm and a resonance frequency of about 75 kHz.
To investigate the possible effect of aqueous media on the morphology of the plasma treated surfaces, these were imaged in deionized water (DIW) and artificial sea water (ASW*) in contact mode using Pointprobe silicon-SPM-sensors (Nanosensors, Germany) with a spring constant of about 0.2 N/m and tip radius lower than 10 nm.
The root-mean-square-roughness (RMS) and the average roughness (Sa) of 10×10 μm^2 scanned areas were calculated using the NanoScope software V530v3sr3.
Scratches on the PDMS surface were produced before imaging either upon tip engagement or application of high forces, depending on the surface mechanical properties. Nanoindentation measurements with five different loads (195, 391, 586, 782, 977 nN) were carried out to estimate both thickness and hardness of the top-most layer generated by the plasma treatment.

2.7. Contact angle measurements

Advancing and receding water contact angle measurements were carried out using a DataPhysics OCA 20 apparatus (DataPhysics, Germany) using the sessile drop method. The results presented are the average of measurements carried out onto 3 replicates. 3 to 5 individual water droplets were measured onto each replicate.
Static contact angle measurements using the captive bubble technique were carried out by attaching sessile air bubbles to the coating surface immersed in ASW* using a microsyringe. The water contact angle was obtained by averaging at least five different measurements done at different locations on each replicate and subtracted to 180°. A minimum of 3 replicates per chemistry were analyzed. The samples were conditioned in ASW* for three hours prior to measurement.

2.8. Biological tests with marine bacteria

The potential of the CF_4 plasma treated PDMS surfaces for inhibition of initial cell attachment and decrease of cell adhesion strength was investigated using biofilms of single marine bacterial species, *Cobetia marina* (collection code DSMZ 4741) and *Marinobacter hydrocarbonoclasticus* (DSMZ 8798). The bacterial strains were kept on sea salt peptone agar at 28°C and stored in the dark. Suspension cultures were prepared from the agar stocks. Briefly, untreated and plasma treated PDMS coated microscope slides were immersed in recirculating sterile (UV treated) deionized water for 7 days and then pre-conditioned in sterile artificial seawater (ASW) for 1 h prior to bacterial assay. Conditioned slides (in replicate) were immersed in 8 ml bacterial suspensions of 0.2 optical density (at 595 nm) in polystyrene quadriPERM plates (Greiner Bio-one Ltd). The plates were incubated at 28°C on a rotary shaker (150 rpm). After 1 h incubation, the slides were gently dipped in sterile seawater (SW) to remove suspended cells. The slides were transferred back into quadriPERM plates containing 8 ml of sterile SW with added growth medium and incubated again for 4 h at 28°C under gentle shaking (150 rpm). At the end of incubation

the slides were again gently rinsed, then placed into slide holders and partially air-dried. The attached biomass was quantified by staining the attached cells with 1.5 μM of the fluorochrome SYTO13 (Invitrogen) and measuring absorption with a Tecan plate reader (GENios, Magellan software) [16].

The adhesion strength of adhered bacteria was quantified using a rotating drum test that was originally designed for the determination of antifouling performance of marine antifouling coatings as described in ASTM D 4939 [17]. After the growth step, replicate slides were mounted on the surface of a custom-made high-speed rotating drum [18]. The drum was then rotated with the surface speed of ~340 m/min for 10 min in SW. This rotational speed of the drum exposes the bacteria to shear stress (turbulent flow), removing bacteria cells from the surfaces. The remaining bacteria were quantified using the stain SYTO13 as described above. The results were expressed as the percentage of bacteria removed or detached by shear stress [(RFU of attached bacteria before release – RFU of bacteria remaining after release)/RFU of attached bacteria before release ×100]. Confidence limits of 95% were calculated.

3. Results and discussion

3.1. Coating preparation

PDMS coatings were prepared on inorganic carriers of variable dimensions for further surface modification by low pressure CF_4 plasma treatment. The PDMS coatings to be used for biological testing were prepared onto standard microscopy slides using an *in-house* developed film preparation setup, which allowed the control of the coating thickness. It has been demonstrated that the coating thickness influences the adhesion strength of fouling organisms [19, 20]. Therefore, the homogeneity and thickness of the PDMS coatings to be tested with organisms were evaluated by optical analysis using the MicroGlider®. The surface of the PDMS coating was very smooth and topographically homogeneous (Figure 3a). The thickness of the coating was determined to be ca. 150 μm (Figure 3b).

3.2. Chemical composition and stability

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemistry upon plasma treatment. Table 1 summarizes the atomic composition of untreated and plasma-treated PDMS sur-

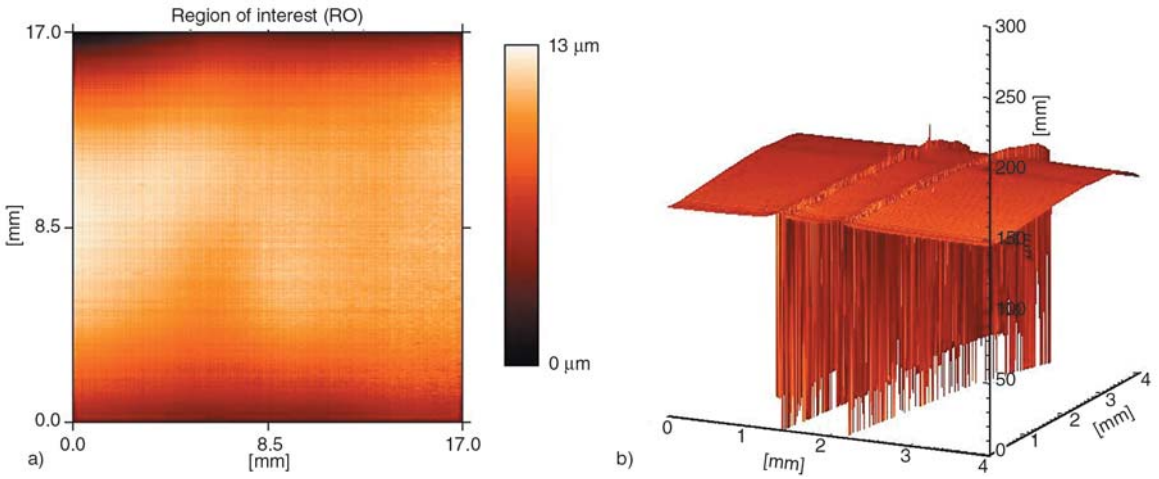

Figure 3. Representative MicroGlider® images of the PDMS coating. a – 2D image of a 17×17 mm² area and b – 3D image of a scratched coating at the edge of the slide (area scanned = 4×4 mm², estimated thickness = 150 μm)

Table 1. XPS data (composition in atomic %) of plasma fluorinated PDMS

Plasma treatment	Composition (atomic %)			
	C 1s	O 1s	Si 2p	F 1s
Untreated[a]	50.0	25.0	25.0	0.0
100 W; 300 s[b]	34.1	12.1	6.5	47.3
50 W; 200 s[b]	35.3	17.9	7.7	39.1
50 W; 100 s[b]	36.5	18.7	9.6	35.2

[a]Theoretical composition.

[b]Data correspond to average of 5-6 samples treated in 2 different batches.

faces for different treatment conditions. The fluorine content increased with power and treatment time up to 47%. For comparison, poly(tetrafluoroethylene) (PTFE), the most common fully fluorinated polymer, has a fluorine content of 66.6%.

To further characterize the chemical structure of the plasma treated PDMS surfaces, high resolution C1s spectra were recorded. It was assumed, that the spectra consist of five components corresponding to aliphatic carbon (285.0 eV), –C–CF– (287.6 eV), –CF– (290.4 eV), –CF_2– (292.0 eV) and –CF_3 (294.0 eV) [21]. To evaluate the C1s spectra of the fluorinated PDMS surfaces obtained under different plasma treatment parameters, a peak deconvolution procedure was applied. Five component peaks with a given shape (Gaussian-Lorentzian ratio 50:50) were set to the energy values mentioned above. The fit procedure was allowed to vary the component energies except 285 eV within a range of ±0.5 eV, the component intensities and a common value for the full width at half maximum.

Deconvoluted C1s spectra of fluorinated PDMS prepared using different plasma treatment conditions are presented in Figure 4. The assumptions of the peak deconvolution model were adequate to describe the shape of the C1s spectra, agreeing with other studies where complex fluorinated polymer systems, as obtained by plasma-based techniques, were investigated [22–24]. All deconvoluted spectra show the full range of differently fluorinated carbon species suggesting a significantly branched and/or cross-linked structure. For the investigated parameter range the relative amount of highly fluorinated species increases continuously with increasing power and treatment time ([CF_3]:[C_xH_y] increased from 0.13 to 0.45, and [CF_2]:[C_xH_y] increased from 0.62 to 1.71 (Figure 4)).

Considering potential underwater applications, and the evidence of chemical re-structuring of silicones upon contacting water [25], we have evaluated the chemical stability of the plasma treated PDMS in aqueous media. Additionally, to assess the influence of ionic strength on the chemical stability of the plasma treated samples, and envisaging the possibility to use these surfaces in marine environment, the fluorine content was determined by XPS immediately after plasma treatment, after storage in ambient conditions, after incubation in recirculating deionized water (DIW), and in artificial sea water (ASW*) for up to one month (Figure 5).

The fluorine content decreased by 6% when samples were simply stored in ambient conditions for

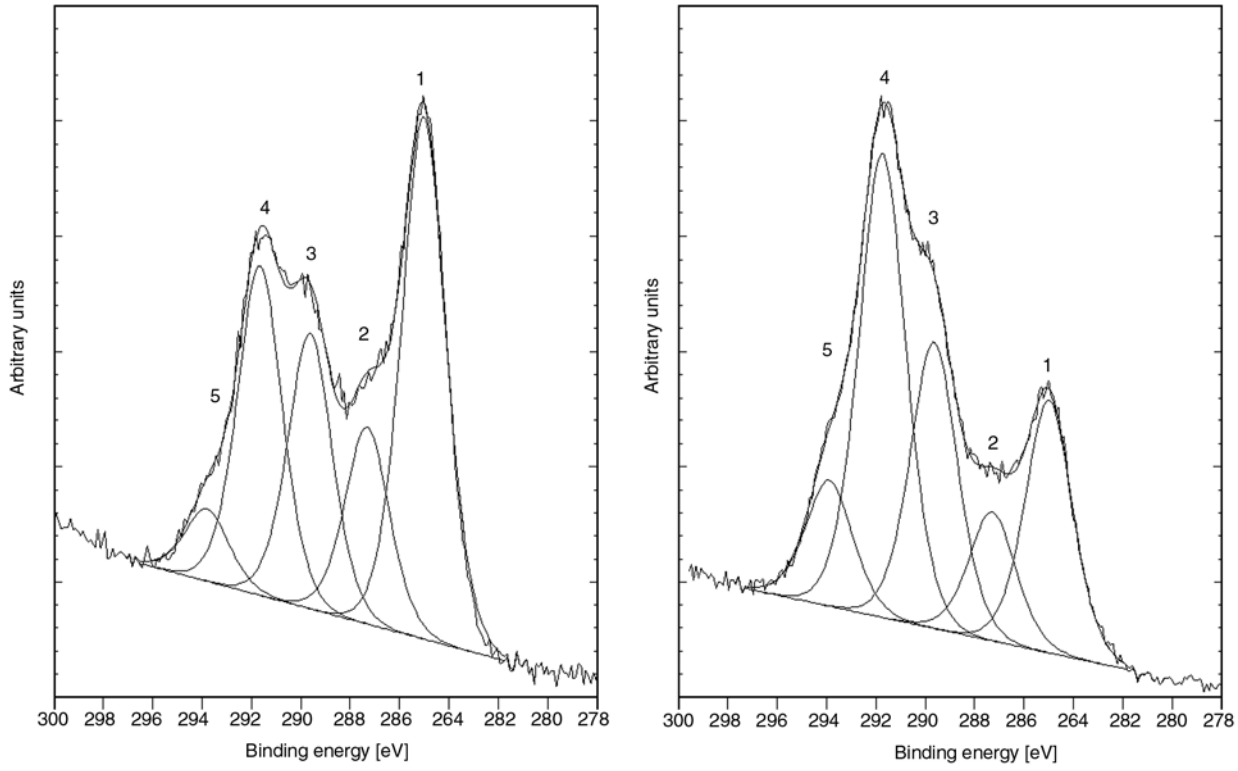

Figure 4. Representative XPS C1s spectra of CF_4 plasma treated PDMS using the parameters: 50 W, 100 s (left), and 100 W, 300 s (right). Peak deconvolution (1) C_xH_y, (2) –C–CF–, (3) –CF–, (4) –CF_2–, and (5) –CF_3.

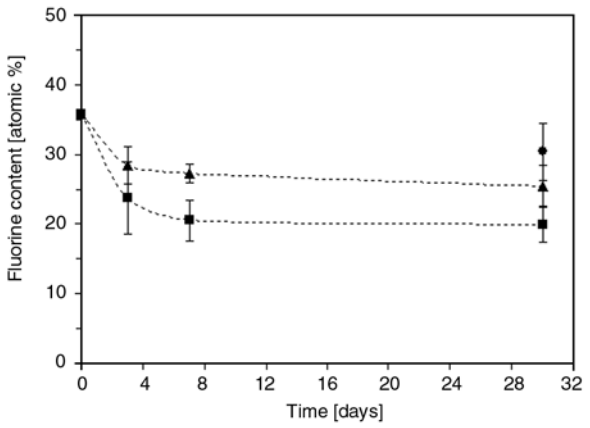

Figure 5. Fluorine content (atomic %) of CF_4 plasma treated PDMS. After plasma treatment (time = 0), after storage in ambient conditions (●), after incubation in recirculating DIW (▲), and after incubation in recirculating ASW* (■).

30 days pointing towards a re-orientation/migration of the fluorine groups away from the surface during aging. The introduction of functional groups onto the surface of silicone has been recognized to lack stability due to the reorganization of silicone elastomers over time [26, 27, 29, 31, 32]. The phenomena of hydrophobic recovery upon PDMS plasma oxidation has been extensively investigated, and explained namely by the reorientation of surface hydrophilic groups towards the bulk and/or reorientation of non-polar groups in the bulk towards the surface, by the diffusion of pre-existing low molecular weight (LMW) species through the bulk to the surface, or migration of created LMW species during treatment to the surface [26]. These same effects are believed to be responsible for the observed decrease of fluorine content on the surface plasma treated PDMS during aging.

When samples were incubated in aqueous media, the fluorine content suffered a steep initial decrease (Figure 5). The fluorine content further decreased after 1 week of incubation, but no additional significant differences could be observed after 4 weeks. This decrease can be explained by re-arrangements of fluorinated groups when the coatings are immersed in water, and by the removal of low molecular weight compounds generated by plasma treatment. The loss of fluorine was significantly higher when the surfaces were incubated in ASW* (loss of 45% of initial content) as compared with DIW (loss of 29% of initial content), revealing the deleterious effect of the presence of salt on the stability of the plasma treated surfaces.

3.3. Morphology

The plasma treatment of polymer surfaces may greatly alter their morphology [28, 29]. For this reason, we have investigated the morphological features of the PDMS surface before and after plasma treatment by atomic force microscopy (AFM) in tapping mode. The surface of the plasma treated PDMS, even using the 'harshest' plasma treatment parameters tested (Figure 6b), was very smooth and comparable to the non-plasma treated surface (Figure 6a). Possible effects of plasma treatment time on surface morphology were investigated for different treatment times (100, 200, and 300 s). The surfaces were very smooth (RMS = 0.5–0.6 nm), no significant morphological differences between treatments could be detected (results not shown).

Additionally, as the exposure of silicones to aqueous media (sea water, phosphate buffered saline) can alter surface morphology [29, 30], the morphological features of the plasma treated PDMS when incubated in DIW and ASW* for 7 days were investigated. Typical height images of the PDMS exposed to the 'harshest' plasma conditions tested when incubated in aqueous media are presented in Figure 6c (DIW) and Figure 6d (ASW*). No morphological changes were observed upon incubation in either of the media tested.

3.4. Mechanical properties

It has been reported that the plasma treatment of PDMS, using a variety of different gases, generates a brittle silica-like layer at the PDMS surface [29, 31–35]. The formation of this hard layer can be explained by the surface oxidation and the etching effects associated with the plasma treatment, exposing some of the silica filler to the surface of the PDMS [29]. In order to investigate the extent of the impact of the CF_4 plasma treatment on the mechanical properties of the PDMS, AFM imaging was performed after indentation measurements and after surface scratching with the AFM tip under high load (Figure 7).

The results showed that the CF_4 plasma treatment resulted in the formation of a harder layer on the

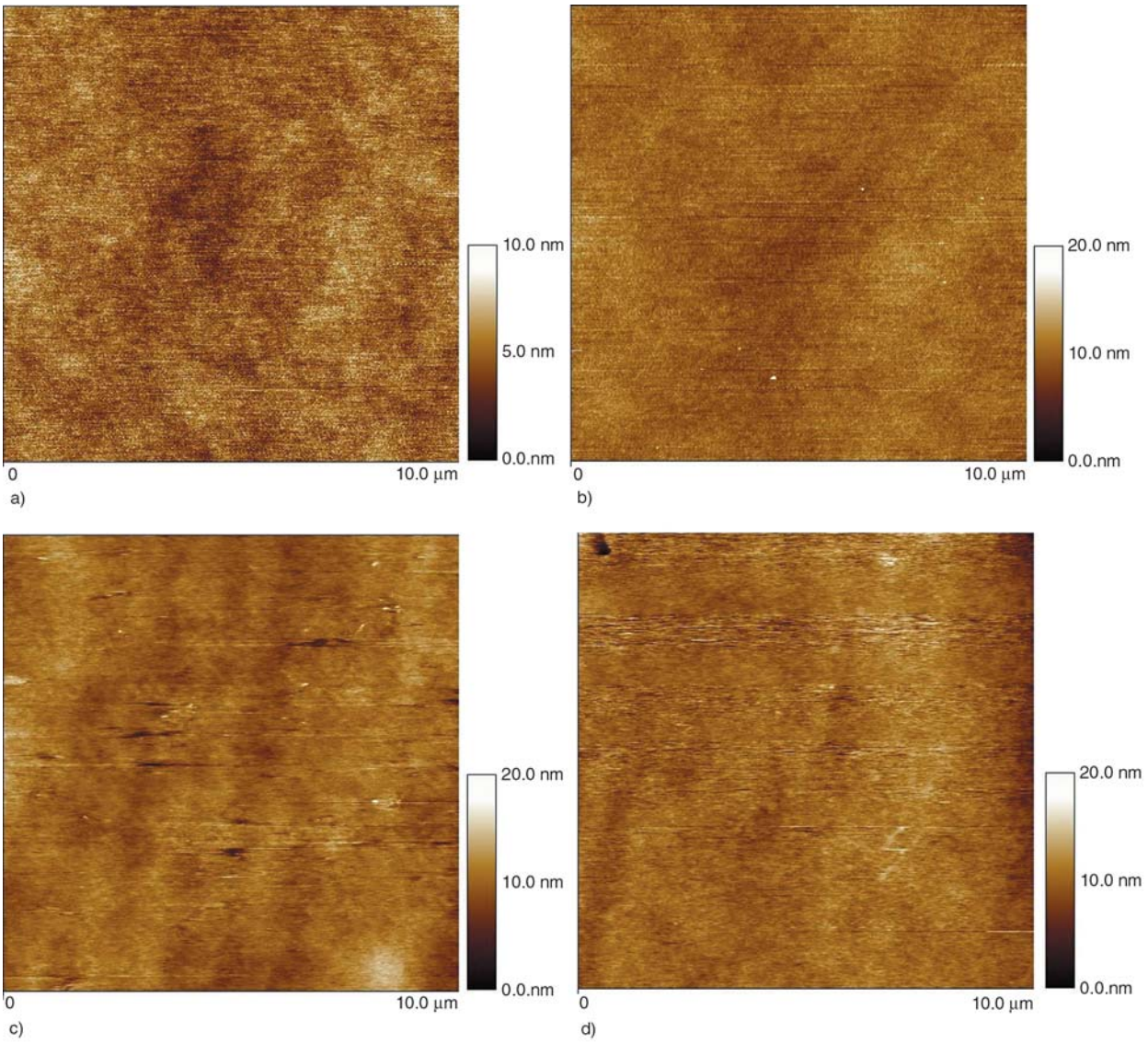

Figure 6. AFM height images of a – PDMS (RMS = 1.15 nm), and b – plasma fluorinated PDMS (plasma treatment conditions: 100 W; 300 s) after preparation (RMS = 1.34 nm); c – after 7 days incubation in recirculating DIW (RMS = 1.33 nm), and d – after 7 days incubation in recirculating ASW* (RMS = 1.58 nm). a) and b) imaging in air using tapping mode, c) imaging in DIW using contact mode, and d) imagining in ASW* using contact mode.

top-most surface of the PDMS, as higher force (>195 nN) was needed to cut through the surface, as compared with the untreated PDMS (data not shown). An apparent wrinkling of the surface was observed (Figure 7) as compared with the characteristic cracking of brittle surfaces [31–33, 35]. The top-most layer seems to elongate under stress, resulting in local thinning of the layer, being reflected on an apparent wrinkling.

The variety and extent of plasma-based surface modification effects, in particular the alteration of elastic properties of PDMS, depend on a multitude of interaction mechanisms, each of them acting on a characteristic depth scale. In low pressure plasma reactors an effect on the scale of several tens of nanometers is most probably attributed to (vacuum) ultraviolet irradiation. As the ultraviolet irradiance of plasma sources with different process gases and different geometries can be different by orders of magnitude [36], the mechanical properties of the treated surface may vary over a certain extend. This possibly explains the difference between our experimental findings (non-brittle surface) and the observations reported in the literature (brittle surface) [31–33, 35].

The differences in mechanical properties of untreated and CF_4 plasma treated PDMS surfaces were further investigated by performing nanoin-

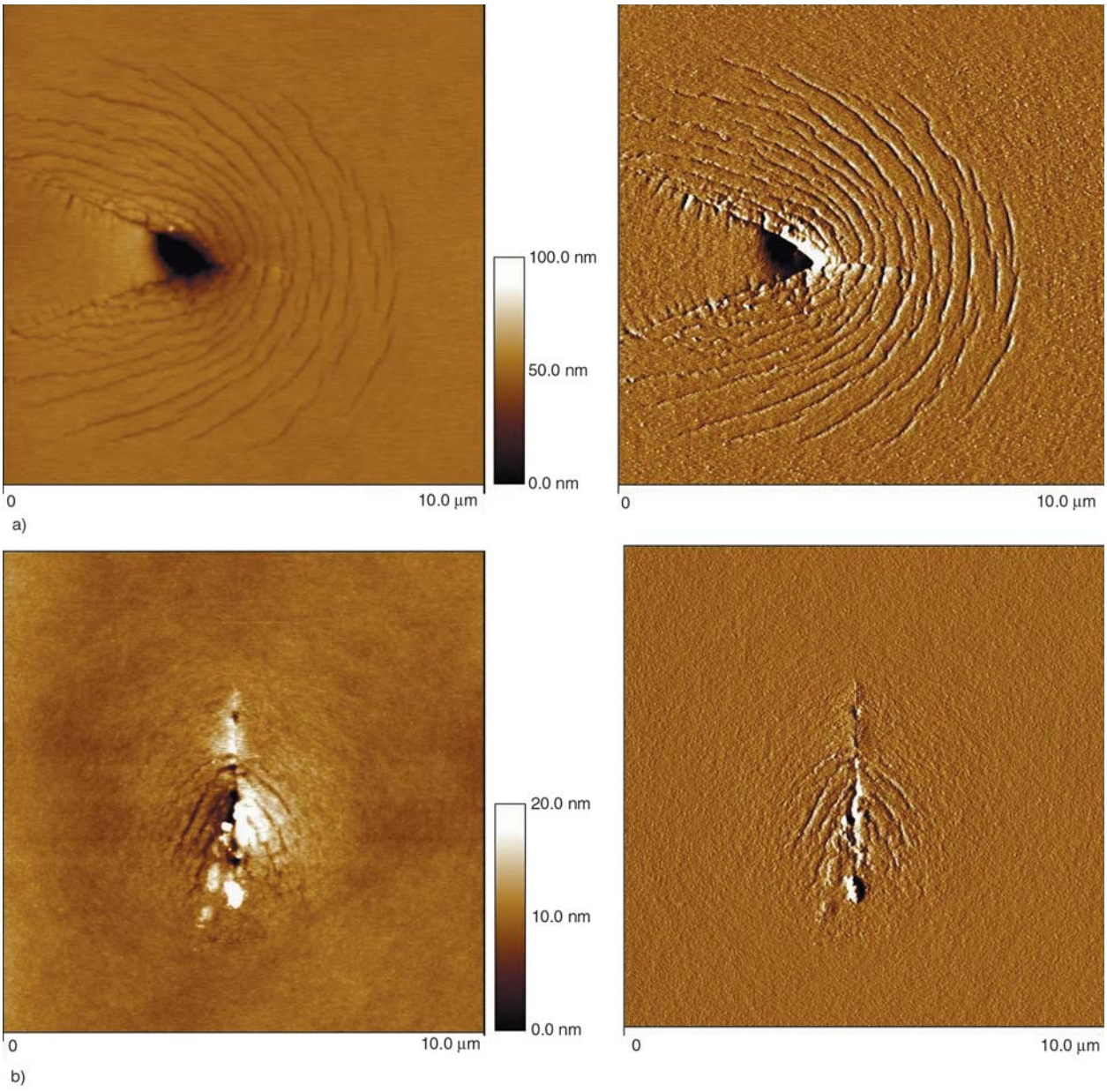

Figure 7. AFM height (left) and amplitude (right) images of plasma fluorinated PDMS (plasma conditions: 50 W; 200 s). Imaging after a – indentation measurement at high force (440 nN); and b – scratching the surface with the AFM tip using high force (440 nN). Imaging in air using tapping mode.

dentation measurements with five different loads. The analysis of the obtained curves allowed to conclude on the presence of a possible double-layer structure, estimate its thickness, and evaluate the hardness of the top-most surface of the PDMS. The force-separation curves of unmodified PDMS clearly differed from the curves obtained for plasma treated PDMS (results not shown). In the case of the plasma treated surfaces, a break in the force-separation curve was observed, indicating the presence of a double layer coating with the mechanical properties of the top-most layer differing from the underlying one. The measured thickness of the top-most layer generated by the plasma treatment and selected indentation results for untreated and plasma treated samples (extracted from load-indentation curves) are presented in Table 2.

The results showed that the thickness of the top-most layer increased with increasing plasma treatment time. The mechanical properties of the top-most layer generated by plasma treatment can be compared for the different plasma conditions tested by comparing the indentation at constant low load. It was observed that when applying a load of 195 nN, the indentation of all plasma treated sam-

Table 2. Thickness of the top-most layer generated by plasma treatment and indentation at low load (195 nN), determined by analysis of AFM load-indentation curves

	Plasma treatment			
	Untreated	**50 W; 100 s**	**50 W; 200 s**	**50 W; 300 s**
Top-most layer thickness [nm][a]	n.a.	180–200	250–280	280–300
Indentation [nm] at load = 195 nN[b]	300 ± 11	112 ± 3	108 ± 3	111 ± 1

[a] data obtained for 2 independent samples

[b] data corresponds to the average of results extracted from 10 independent curves (± standard deviation)

ples was below 180 nm (i.e. within the thickness of the top-most layer) allowing the characterization of the top-most surface of the plasma treated PDMS. A significantly higher indentation was measured for the untreated PDMS as compared with the plasma treated PDMS, indicating that the top-most layer generated by the plasma treatment was characterized by a higher Young modulus. No significant differences could be detected between the different plasma conditions tested. This suggests that the plasma conditions tested only had a significant effect on the thickness of the generated top-most layer but not on its mechanical properties. When applying loads higher than 195 nN, the indentation was deeper than the thickness of the top-most layer, resulting in scattered indentation data due to the contribution of the bulk PDMS.

3.5. Wettability

The extent of changes in the wetting properties of the PDMS surface generated by CF_4 plasma treatment was evaluated by measuring advancing and receding water contact angles using the sessile drop technique (Table 3). Contrary to what would be expected, the CF_4 plasma treatment resulted in a more hydrophilic surface as compared with the untreated surface. This can be explained if we consider that the effect of introduction of fluorine is overcompensated by side effects associated with plasma treatment as surface oxidation. Furthermore, the fluorine groups originally at the surface will re-orient towards the bulk exposing moieties rich in oxygen to the surface, resulting in a decrease of the measured water contact angle. The contact angle hysteresis increased after plasma treatment, possibly due to chemical heterogeneities [37] introduced by the plasma treatment and/or due to surface reorganization [38].

Table 3. Advancing and receding water contact angles measured by the sessile drop technique

Plasma treatment	Advancing water contact angle [°]	Receding water contact angle [°]
Untreated	118.7 ± 1.4	85.6 ± 2.8
100 W; 300 s	100.9 ± 1.1	43.9 ± 5.3

Table 4. Static water contact angle measured using the captive bubble technique

	Plasma treatment	
	Untreated	**100 W; 300 s**
Static water contact angle [°]	95.2 ± 0.9	124.7 ± 1.3
		

Considering the potential use of these surfaces in the marine environment, and the effect of sea water on the surface properties of silicones [39, 40], we have measured static water contact angles on untreated and plasma treated surfaces using captive air bubbles in ASW* (Table 4). The captive bubble results in ASW* were in good agreement with the data obtained using the sessile drop technique. The PDMS surface was found to be more hydrophilic after CF_4 plasma treatment.

3.6. Marine bacteria: attachment and adhesion strength

The effect of the introduction of fluorine into the PDMS surface on the inhibition of initial attachment and on the adhesion strength of the marine bacteria *Cobetia marina* and *Marinobacter hydrocarbonoclasticus* was investigated. These two species were selected as they are characterized by distinct surface energies: *Cobetia marina* is hydrophilic, and *Marinobacter hydrocarbonoclasticus* is hydrophobic [41]. The results of the assays on glass control slides, untreated PDMS coatings, and CF_4 plasma treated PDMS with a fluorine content of 47% (atomic %) are presented in Figure 8.

The attachment of both *Marinobacter hydrocarbonoclasticus* and of *Cobetia marina* were dramati-

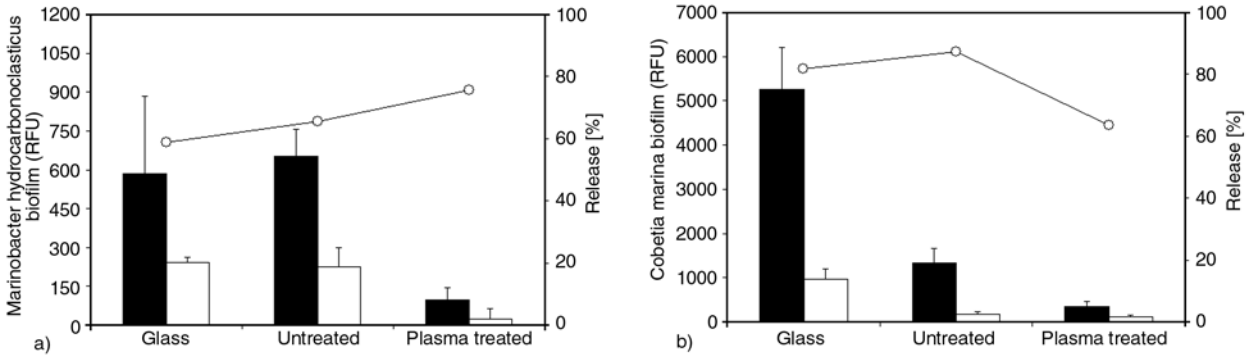

Figure 8. Marine bacterial biofilms of a – *Marinobacter hydrocarbonoclasticus* and b – *Cobetia marina* on glass, untreated PDMS, and CF_4 plasma treated PDMS. Bacterial biofilm formation (black bars) and remaining marine bacteria biofilm after rotation at 340 m/min for 10 min (white bars). The release percentages (O) represent the percentages of biofilm removal upon exposure to shear. N = 45; error bars = 2×standard error derived from arcsine-transformed data.

cally reduced when introducing fluorine into the PDMS coating. Bacterial adhesion to surfaces has been attributed to many factors, including surface chemical composition [42, 43], surface hydrophilicity [44], surface roughness [45], and surface mechanical properties [46]. As no significant differences in surface roughness were detected between untreated and plasma treated samples (Figure 6), the differences observed in bacteria attachment cannot be attributed to differences in surface morphology. The plasma treatment has altered the mechanical properties of the top-most surface of the PDMS (Table 2). A positive correlation between substrate stiffness and the initial attachment of the bacteria *Staphylococcus epidermis* has been reported [46]. However this correlation does not apply in the case of the present study as lower bacteria attachment was observed for the plasma treated (harder) surface. Recent bacteria studies using silicon oxide coatings deposited by plasma-assisted chemical vapour deposition (PACVD) methods showed that the attachment of *Pseudomonas fluorescens* decreased with increasing the surface water contact angle, the same trend being observed for *Cobetia marina* [41]. An opposite effect was observed in our experiments. Concerning the attachment of *Marinobacter hydrocarbonoclasticus*, it was observed to increase with increasing the water contact angle of the silicon oxide surfaces [41], being in good agreement with our observations. The mechanism of bacteria adhesion is very complex, depending not only on the surface physicochemical properties but also on the properties of the bacteria. Although hydrophobicity has been generally considered to play a significant role in bacteria adhesion, our results indicate that the nature of the surface functional groups is critical in defining the interaction between substrate and bacteria. The mechanism of antimicrobial action provided by the presence of fluorinated species at the plasma treated PDMS surface is however unknown and deserves further investigations.

The adhesion strength of *Marinobacter hydrocarbonoclasticus* decreased upon introduction of fluorine into the PDMS surface (% removal increases from 65 to 76%), while the adhesion strength of *Cobetia marina* increased after plasma treatment (% removal decrease from 87 to 64%). The easier detachment of hydrophobic bacteria (*Marinobacter*) from more hydrophilic surface (plasma treated) and of hydrophilic bacteria (*Cobetia*) from more hydrophobic surface (untreated) support that both the native properties of the individual strain of bacteria and the chemical composition of the surface determine bacteria adhesion strength [47].

4. Conclusions

Low pressure CF_4 plasma can be used to successfully introduce fluorinated groups into PDMS surfaces. The plasma treatment generated a smooth, non-brittle layer at the top-most surface of the PDMS, with very high fluorine content and possibly a significantly branched and/or cross-linked structure. Stability tests revealed a loss of fluorine in the plasma treated surface upon incubation in aqueous media, possibly due to the removal of low molecular weight (LMW) compounds generated by

plasma treatment, and/or to the re-orientation of the fluorine moieties away from the surface. As a consequence of oxidation effects associated with the plasma treatment, and the re-orientation of fluorinated groups, the PDMS surface was more hydrophilic after plasma treatment. The antifouling potentialities of PDMS towards two species of marine bacteria was improved after CF_4 plasma treatment suggesting that the approach described for the fluorination of PDMS surfaces may be applied to minimize microbial adhesion.

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