Influence of Chemistry and Topology Effects on Superhydrophobic CF₄-Plasma-Treated Poly(dimethylsiloxane) (PDMS)

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Superhydrophobic surfaces are gaining considerable interest in a lot of different applications, and nonetheless, precise control over the wettability properties of such surfaces is still a challenge due to difficulties when controlling the effects independently induced on superhydrophobicity by the chemical and topological surface characteristics. We have fabricated engineered superhydrophobic surfaces onto poly(dimethylsiloxane) (PDMS) substrates by means of suitable CF₄-plasma treatments. These treatments allowed the modification of both the morphological properties of the PDMS surface, due to a preferential etching of certain components of its macromolecules, and the chemical ones, by the deposition of a fluorinated layer. Chemical effects were separated from topological ones by performing a double replica molding process of the CF₄-plasma-treated surfaces. This allowed us to obtain positive copies of the structured surfaces without the overlaying fluorinated coating affecting the surface chemistry. Such replicated surfaces showed a decrease of the contact angle if compared to the treated ones and therefore evidenced chemistry's weight in superhydrophobicity effects. In particular, we found that, for highly dense columnar-like PDMS microstructures, the effect of the plasma-deposited fluorinated layer covering surfaces produces an enhancement of the contact angle of about 20°.

1. Introduction

Controlling wetting properties of solid surfaces is currently the focus of considerable research in many practical applications ranging from the development of self-cleaning surfaces^{1–4} to droplet-based (“digital”) microfluidics.^{5–7} As it is well-known, the wettability of a solid surface depends on two main factors: surface energy γ and topography. The surface energy γ is an intrinsic property of the material that stems from asymmetric forces acting on molecules at the interface between different phases, and it can be controlled by chemical modification. In particular, nonwettable surfaces, showing a high contact angle (CA), are usually obtained with fluorinated copolymer-based coatings characterized by low values of γ . However, even flat surfaces covered with very low γ coatings showed a contact angle which did not exceed 120°. Generally, very large contact angles and superhydrophobic behavior can be determined only if low γ and elevated roughness are simultaneously present. The effect of the surface roughness on the wettability and in particular

on the apparent contact angle of a sessile droplet was modeled more than half a century ago.^{8,9} Studies on the lotus leaf, the most famous superhydrophobic surface found in nature, revealed that its surface is composed of heterogeneously rough hills and valleys coated with low γ waxy materials.^{10,11} The hills and valleys ensure that the area of real contact available to water is highly reduced, while the hydrophobic waxy materials prevent water from penetrating into the valleys, so that the CA of the drop is determined almost solely by the surface tension of the liquid. The most evident result is that water cannot wet the surface of lotus leaves, and spherically formed water droplets roll off the surface. Therefore, the fundamental mechanism of the lotus effect suggests that both chemical modification (leading to the low surface energy) and surface morphology (surface roughness) are important factors in determining the hydrophobicity of surfaces. Up to now, a wide variety of techniques have been developed to produce synthetic superhydrophobic surfaces (showing CA > 150°) based on micro- and/or nanotexturing of surfaces of various materials. Coating substrates with TiO₂ nanoparticles mixed with fluorinated copolymers,¹² electrochemical deposition of gold¹³ and silver¹⁴ aggregates followed by chemisorption of a monolayer of *n*-dodecanethiol, electrodeposition of copper combined with lithography¹⁵ or copper wet etching,¹⁶ close-packed polystyrene

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microsphere topography,¹⁷ casting of polymer solutions under humid conditions,¹⁸ mechanical assembly of monolayers on elastomeric surfaces,¹⁹ and a gelation process for polypropylene²⁰ and tetraethyl orthosilicate mixed with an acrylic polymer²¹ are just a few of the most recent methods used for the production of superhydrophobic surfaces. A lot of plasma techniques have also been employed with many different polymeric materials to create desirable surface characteristics while preserving bulk properties. For this purpose, several authors^{22–28} report CF₄-plasma treatments to achieve fluorinated polymer surfaces exhibiting low surface energy, chemical inertness, and low coefficient of friction. In all these cited cases, superhydrophobicity is induced by the simultaneous modification of both the chemical and morphological properties of the surface without a clear identification of the effect of each single factor. Therefore, the knowledge of the relative weight of each component is a key factor to establish an effective design criterion to tailor wetting properties of a synthetic surface.

In the present work, we evaluate, for the first time, the relative influence of surface chemistry and topology in determining the superhydrophobic behavior of poly(dimethylsiloxane) (PDMS) surfaces. We first generated tailored PDMS microstructured fluorinated surfaces by exposing the surface to a properly controlled CF₄-plasma treatment, and then we performed a double replica molding process to faithfully reproduce such topographic features onto nonfluorinated PDMS surfaces.

2. Theoretical Background

At the equilibrium configuration, the contact angle of a liquid drop placed on a solid substrate is given by the so-called Young's equation

$$\cos \theta_0 = \frac{\gamma_s - \gamma_{SL}}{\gamma_L} \quad (1)$$

where γ_s and γ_{SL} are, respectively, the surface energies of the solid against air and liquid and γ_L is the surface energy of the liquid against air.²⁹

Equation 1 provides the value of the static contact angle for given surface energies, but it does not supply any information on the nature of the intermolecular forces giving rise to such drop macroscopic behavior. This information can be explicated by using the Good–van Oss approach,^{30,31} which gives the most accurate evaluation of the surface energy. According to this approach, the surface energy includes three main contributions according to the following equation:

$$\gamma = \gamma^{LW} + 2(\gamma^+ + \gamma^-)^{1/2} \quad (2)$$

where γ^{LW} is the contribution due to the apolar or Lifshitz–van der Waals interactions of molecules at the interface, while γ^+ and γ^- represent, respectively, the electron acceptor (or Lewis acid) and electron donor (or Lewis base) contributions of the polar interactions. For a drop of water at equilibrium with a solid surface γ_s^{LW} , γ_s^+ and γ_s^- can be calculated by using the modified Young–Duprè equation

$$\gamma_L(1 + \cos \theta) = 2[(\gamma_s^{LW} \gamma_L^{LW})^{1/2} + (\gamma_s^+ \gamma_L^-)^{1/2} + (\gamma_s^- \gamma_L^+)^{1/2}] \quad (3)$$

by performing liquid–solid contact angle measurements (θ) for three characterized liquids, typically water, diiodomethane, and ethylene glycol.

The Good–van Oss approach has been successfully used by Tsibouklis³² to determine the molecular design requirements to obtain ultralow surface energy polymers. By measuring the surface energy components (as described in eq 2) associated with several perfluorinated polymers, Tsibouklis was able to individuate the fundamental macromolecular structural features determining their wetting behavior. Therefore, by properly manipulating the surface chemistry of polymeric materials, it is, in principle, possible to reduce their surface and interfacial energy and, according to Young's equation, to increase the contact angle. However, Young's equation is valid only in the case of flat solid surfaces. If we consider a rough solid surface, with typical roughness features smaller than the size of a droplet (so that the roughness distribution does not affect the contact angle), the effective interfacial tension may be a complex function of the surface roughness. Considering a droplet upon a rough surface, eq 1 should be modified as predicted by Wenzel⁸ as follows:

$$\cos \vartheta_W = \frac{A_{SL}}{A_F} \cos \vartheta_0 = R_f \cos \vartheta_0 \quad (4)$$

where θ_W is the contact angle for the rough surface and R_f is the roughness factor defined as the ratio between the total surface area of the rough surface A_{SL} and the projected area of the rough surface or the equivalent flat solid–liquid surface area A_F .

Equation 4 shows that if the liquid wets a flat surface ($\cos \theta_0 > 0$), it will also wet the rough surface with a contact angle of $\theta_W < \theta_0$, since $A_{SL}/A_F > 1$. Furthermore, for nonwetting liquids ($\cos \theta_0 < 0$), the contact angle with a rough surface will be larger than that with the flat surface, $\theta_W > \theta_0$.

However, even though more accurate than Young's model, the Wenzel equation does not predict the behavior of nonwetting liquids that cannot penetrate into surface cavities with large slopes, resulting in the formation of air pockets. In these systems, the solid–liquid contact zones are located at the peaks of the asperities, whereas the air pockets and solid–air contact zones are in the valleys and the solid–liquid contact area will not further increase with increasing roughness.³³ Similar cases were analyzed by Cassie and Baxter⁹ who extended the Wenzel equation to inhomogeneous systems with a liquid–air interface (liquid/ambient) and a flat composite interface under the droplet involving solid–liquid, liquid–air, and solid–air interfaces. For these systems, Cassie–Baxter calculated a contact angle given by

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$$\cos \vartheta_{\text{CB}} = \varphi_{\text{S}}(\cos \vartheta_0 + 1) - 1 \quad (5)$$

where φ_{S} is the fraction of the projected planar area of the drop in contact with the solid.

According to eq 5, in the limit of high R_{f} , φ_{S} approaches zero, and hence, θ approaches 180°.

The conditions under which the composite interface forms were studied by Johnson and Dettre³⁴ who showed that the homogeneous and composite interfaces correspond to the two metastable states of a droplet. Even though it may be geometrically possible for the system to become composite, it may be energetically profitable for the liquid to penetrate into valleys between asperities and to form the homogeneous interface. The geometrical conditions for a surface, under which the energy of the system has a local minimum and a composite interface is present, were formulated by Marmur.³⁵

3. Experimental Section

Materials. A commercial poly(dimethylsiloxane) elastomer kit (Sylgard 184) was purchased from Dow Corning. The silicone base and its curing agent were thoroughly mixed in a 10:1 weight ratio. Air bubbles trapped in the prepolymer mixture were removed by degassing at 40 mTorr for 20 min. Flat films were prepared using an horizontal spacer mold with a cavity formed by a steel ring on a glass substrate. The degassed prepolymer mixture was poured into the cavity and further degassed at 40 mTorr for another 20 min. The prepolymer was then cured at 140 °C for 15 min to produce 2 mm thick PDMS flat sheets. Before use, the cured PDMS slabs were cleaned in successive ultrasonic baths with DI for 15 min and then dried under vacuum of 40 mTorr at 60 °C for 24h.

CF₄-Plasma Treatment. After thermal cross-linking, the PDMS slabs were removed from the mold and treated with CF₄-plasma. This allowed us to increase the roughness due to preferential etching of certain components of the polymeric material in fluorine-containing plasmas.³⁷ To enhance the fluorination rate, an argon plasma pretreatment was performed. As is well-known, plasma treatment using Ar, due to its high atomic number, can effectively create stable free radicals on a polymer surface.³⁸ When subsequently exposed to CF₄-plasma, the surface free radicals can rapidly react with the F-containing plasma radicals, accelerating fluorination. In our study, a 5 min Ar-plasma pretreatment was carried out before the CF₄-plasma treatment. Plasma treatments were performed in an IONVAC inductively coupled plasma (ICP) reactor (PGF 600 RF HUTTER). The samples were placed into the chamber, followed by evacuation to 40 mTorr. Ar gas was introduced at a flow rate of 50 sccm (standard cubic centimeter per minute), and the glow discharge was ignited at 200 W. CF₄ was then introduced at a flow rate of 16 sccm, and different treatments were performed at different plasma conditions (by changing pressure, power, and exposure time). Upon completion of CF₄-plasma treatment, to reduce the physical adsorption of CF₄ on the surface, each sample was purged with N₂ for 30 min under vacuum conditions.

Characterization. The surface wetting properties were evaluated by using an OCA 20 system from DataPhysics. Water contact angle (CA) measurements were obtained using the sessile drop method by averaging the measurements on 10 different positions of the examined surface.

X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Physical Electronics (PHI) 5800-01 spectrometer. A monochromatic Al K α X-ray source was used at a power of 350 W. Due to the insulating nature of the samples high flux, a low-energy distribution cold cathode flood gun neutralizer was used during all measurements. Spectra were obtained with pass energies

of 58.7 eV for elemental analysis (composition) and 11.75 eV for the determination of the chemical species. The pressure in the analysis chamber of the spectrometer was 1×10^{-9} Torr during the measurements. To compensate for surface-charging effects, the calibration of the binding energy (BE) scale was made with reference to the BE of 284.6 eV of the adventitious carbon. This does not differ significantly from the BE of the C–Si bond at 284.4 eV^{39,40} that contributes as well to the C 1s signal. Spectra were collected at a photoelectron takeoff angle of 45° with respect to the sample surface. The quantitative evaluation of each peak was obtained by dividing the integrated peak area, after Shirley background subtraction, by atomic sensitivity factors, which were calculated from the ionization cross sections, the mean free electron escape depth, and the measured transmission functions of the spectrometer by using the PHI Multipak 6.1 software.

The surface morphology of PDMS samples before and after the replica molding process was characterized by both scanning electron microscopy (SEM) and atomic force microscopy (AFM). In the first case, the images were taken with a Leica Stereoscan-440 instrument. An electron beam evaporator (Temescal Supersource) was used to coat a conductive layer of gold onto the PDMS surfaces before observing the microstructure. AFM measurements were carried out with a SMENA MT-DTA atomic force microscope. All scans were performed in air using the tapping mode. To describe in detail the topographic modifications of plasma-treated PDMS surfaces, all acquired AFM images were analyzed using the detection software SPIP and several statistic parameters were used to characterize their topography. Among them, Wenzel and Cassie–Baxter coefficients, respectively, R_{f} and φ_{S} , were evaluated as follows:

(i) The Wenzel coefficient R_{f} , denoted as the ratio between the surface area (taking the z -height into account) and the area of the flat xy -plane, was calculated as

$$R_{\text{f}} = 1 + \frac{\left(\sum_{k=0}^{M-2} \sum_{l=0}^{N-2} A_{kl} \right) - (M-1)(N-1) \delta x \delta y}{(M-1)(N-1) \delta x \delta y} \quad (6)$$

where

$$A_{kl} = \frac{1}{4} \left| \sqrt{\delta y^2 + (z(x_k, y_l) - z(x_k, y_{l+1}))^2} + \sqrt{\delta y^2 + (z(x_{k+1}, y_l) - z(x_{k+1}, y_{l+1}))^2} \right| \times \left| \sqrt{\delta x^2 + (z(x_k, y_l) - z(x_{k+1}, y_l))^2} + \sqrt{\delta x^2 + (z(x_k, y_{l+1}) - z(x_{k+1}, y_{l+1}))^2} \right| \quad (7)$$

(ii) The Cassie–Baxter coefficient φ_{S} , denoted as the surface fraction covered by the column tops, was extrapolated by performing a grain analysis with a threshold segmentation of AFM images.⁴¹ In this method, the “islands” left when the image landscape is flooded to the threshold level are counted as grains. The detection level defines the minimum z -value needed for a pixel to be regarded as part of a segment. To improve the detection performance, we first equalized the z -values of our images by simply subtracting the mean value of the pixels in the local neighborhood. We then chose a fixed detection level, so only pixels having a z -value above this detection level were regarded and higher hill peaks were considered. By performing this grain analysis, we were able to calculate the percentage of area covered by detected grains, that is, the surface fraction covered by the column tops that correspond to the Cassie–Baxter coefficient φ_{S} . An example of this procedure is reported in Figure 1.

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Figure 1. Grain analysis with threshold segmentation of a 10 min CF₄-plasma-treated sample AFM image. (a) 2D image of surface topography. (b) Having defined the height threshold for peak detection, all values above this threshold are considered as peak values. The detection level works in correspondence with a color scale editor, where the lower color limit of the color bar reflects the detection level. In this way, it is also possible to get direct visual feedback from the colors in the topographic image. The detected peaks are marked with contour lines in different colors and (c) filled with high contrast colors for easy identification. (d) All the detected peak areas are included in the histogram, and the cumulative integral is used to calculate the fraction of projected area φ .

4. Results and Discussion

Control of Plasma Conditions for Tailoring PDMS Topography. Tuning of the morphological features was possible by adjusting the parameters affecting plasma treatment conditions. We started investigating the influence of treatment strength on PDMS surface topography. In particular, we first compared the effect of a “soft CF₄-plasma treatment”, characterized by relatively high pressure (70 mTorr) and low power (70 W), with that of a “hard CF₄-plasma treatment”, characterized by relatively low pressure (20 mTorr) and high power (200 W), on an initially flat sample. In both cases, CF₄ flux was kept constant at a 16 sccm value, as well as Ar-plasma pretreatments conditions. The plasma exposure time was instead varied in a range from 10 to 80 min.

Upon AFM analysis, both treated samples showed a roughened surface with features ranging from a few hundred nanometers to a few micrometers depending on exposure time. However, the topographies appeared to be very different. AFM images of two 10 min-treated samples are reported in Figure 2. In the “soft-

treated” one, we observed the formation of periodic 2D wavy structures similar to spinodal dewetting formations. The formation of similar structures during plasma treatment of PDMS is a well-known phenomenon, and it was already observed by several authors.^{42–44} Such phenomenon is due to the mechanical stress introduced by the mismatch between the thermal-expansion coefficients of the surface layer and bulk material. Each PDMS surface was characterized by a combination of microstructures with a fluorocarbon (FC) coating, as a result of the plasma treatment. Within “soft-treatment” conditions, the weight of fluorocarbon deposition was prevalent on the etching process, causing the generation of 2D quasi-ordered structures such as the ones that are common in the deposition of hot films on PDMS.

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Figure 2. AFM images of the PDMS samples after a 10 min CF_4 -plasma treatment. The soft-treated surface (a) shows quasi-periodic 2D wavy microstructures; the hard-treated surface (b) shows random isotropic columnar-like microstructures.

On the other hand, in the hard-treated sample, the observed microstructures had random hill distribution. In this case, due to the stronger etching, the sputtering effect is reduced and isotropic surfaces can be obtained.

To achieve columnar-like structures and major control of the geometrical parameters, we chose to use the hard-treatment approach. We performed a series of different CF_4 -plasma treatments and peak heights, and their separation distance were tuned. Having evaluated different combinations of the parameters, we finally established the use of a fixed set of plasma conditions (16 sccm CF_4 flow, 40 mTorr pressure, 170 W power) and we varied the exposure time from 10 to 80 min. In this way, we were able to fabricate a set of patterned surfaces with the same quasi-ordered features distribution but different dimensions.

Similar to many engineered and natural rough surfaces, these structures were characterized by a Gaussian height distribution function and an exponential autocorrelation function.⁴⁵ In particular, we described our rough PDMS surfaces in terms of the following three meaningful parameters: (i) the root-mean-square roughness R_q ; (ii) the peak-to-peak mean value of the Gaussian distribution of asperity heights R_y , responsible for the vertical scale; and (iii) the autocorrelation length β^* , responsible for the horizontal scale. The autocorrelation function $G(r)$ is

determined as the product of topography heights in two points, separated from each other by a fixed distance r , averaged for a sufficiently large area. We observed that for all samples the autocorrelation function exhibits a plateau region after which a change in the graph slope is observed. It denotes the so-called correlation length β^* and corresponds to the characteristic distance over which the spike–spike distances “know about” each other (or they are correlated). An example is shown in Figure 3, where the topography of a 20 min plasma-treated sample is reported. The surface exhibits a forest of quasi-periodic columnar-like protrusions (a) having a height distribution function (d) that can be approximated to a Gaussian distribution with a mean value $R_y \approx 1.55 \mu\text{m}$ and a full width at half-maximum (FWHM) $\approx 1 \mu\text{m}$. The autocorrelation function’s profile (c) shows two linear regions separated by a small substantially horizontal stretch (plateau-zone) that corresponds to the characteristic wavelength of the quasi-periodic topography.

This set of morphological parameters was calculated for every treated sample. As we reported in Figure 7, both the mean value of height distribution and the autocorrelation length increase linearly within the first 60 min with a rate of $\approx 65 \text{ nm/min}$ and $\approx 50 \text{ nm/min}$, respectively; after the first 60 min, the increase is slower. In particular, the mean peak-to-peak height seems to converge toward a saturation value of less than $4.5 \mu\text{m}$.

Chemical Composition of CF_4 -Plasma-Treated Surfaces.

To evaluate the compositional changes on the poly(dimethylsiloxane) surface after CF_4 -plasma etching, XPS analysis was performed. The results of the quantitative chemical analysis are reported in Table 1 and Figure 4. The initial surface composition of the elastomer $\text{Si}:\text{O}:\text{C} = 1:1:2$ changed to about $1:1.1:1.65$, and the surface of the etched specimens became enriched with fluorine.

As reported in previous studies,^{23,46} the reactive species in CF_4 -plasma are primarily fluorine atoms with a small concentration of complex fluorocarbon species. Fluorine atoms and F-substituted methyl species can graft onto a polymeric surface via hydrogen replacement and the opening of unsaturated bonds to form CF , CF_2 , and CF_3 functionalities, whereas high molecular-weight fluorocarbon species can form a film of thin fluorocarbon macromolecules on the substrate surface. In the case of PDMS, however, $-\text{CH}_3$ replacement is highly probable, considering the lower bond energy of $\text{C}-\text{Si}$ than that of $\text{C}-\text{H}$.⁴⁷ So, if hydrogen atoms in the PDMS backbone were completely substituted by fluorine, a theoretically maximal F/C ratio of 3 could be obtained. However, as evident from data shown in Table 1, this maximal value is not reached, and the fluorine atomic percentage (ranging from 3.91% to 5.25%) seems to remain substantially constant for treatment exposure times ranging from 20 to 80 min. It has been pointed out in fact that, besides CF_4 -plasma fluorination, ablation or etching also occurs and the two reactions seem to be parallel and competitive. The relative rates of fluorination and ablation are dependent on treatment time under constant power supply for a fixed polymer.²⁶ At first, fluorination predominates over ablation so that the fluorine content increases rapidly. Beyond a critical treatment time, the two reactions reach a dynamic near-equilibrium with a slow variation of the F percentage on the surfaces. This means that, after 20 min of CF_4 -exposure, surface fluorination has practically reached its equilibrium value and a further exposure does not substantially affect the surface chemical composition or that, for plasma process conditions we implemented, the critical treatment time determining such dynamic

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Figure 3. AFM analysis of the 20 min CF₄-plasma-treated PDMS samples. (a) 3D image of surface topography. (b) Distribution map of the height–height correlation function and (c) its profile on the selected section: the autocorrelation length β^* is in the changing-slope zone, and its value is assumed to correspond to the abscissa of the local minimum $\approx 1.1\ \mu\text{m}$. (d) Histogram of height distribution: the mean value R_y is $1.55\ \mu\text{m}$.

Table 1. Elemental Composition of CF₄-Plasma-Treated PDMS Surfaces as Determined by XPS

sample	C 1s (%)	O 1s (%)	F 1s (%)	Si 2p (%)
reference	50.1	25.6		24.3
20 min	42.32	27.77	4.66	25.26
30 min	42.08	28.46	3.91	25.55
40 min	42.02	27.67	5.25	25.05
60 min	41.95	28.04	4.39	25.60
80 min	41.12	28.80	4.82	25.26

near-equilibrium is less than 20 min. Furthermore, it should be mentioned that the analysis depth in the present XPS measurements is about 5 nm. The resulting chemical composition reflects not only the top layers on the surface but also a few underlying layers. Thus, it may be possible that, after the replacement of $-\text{CH}_3$ with fluorinated methyl groups (e.g., $-\text{CF}_3$ species) on the surface top layers, this process does not continue further in the case of moderate exposure times; accordingly, the chemistry of the underlying layers remains unchanged.

To better clarify the chemical changes which occur on the surface, we have reported below (Figure 5) the high-resolution spectra obtained in the binding energy (BE) range of F 1s of four treated samples. The spectra obtained for all the specimens are similar. The results of the deconvolution procedure indicated the presence of two different fluorine chemical states at approximately 687.5 and 685 eV. The former energy value is related to the fluorination of methyl groups and might be assigned to CF_2 or CF_3 , with the latter being due to the presence of Si–F bonds associated with the formation of fluorosilyl species on silicon surfaces.^{48,49}

Figure 4. XPS survey spectra for PDMS before (ref) and after several CF₄-plasma treatments performed in the same chamber conditions but for different exposure times.

In this range of treatment times, F–C bonding dramatically predominates over F–Si. The $[\text{F–C}]/[\text{F–Si}]$ ratio varies from 7 to 3 as the time of treatment increases from 20 to 80 min. Although no well-defined relationship between the $[\text{F–C}]/[\text{F–Si}]$ ratio was found with respect to the exposure time, an increase

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Figure 5. Fluorine 1s photoelectron spectra of PDMS after 20, 30, 40, and 80 min CF_4 -plasma treatment.

of the Si–F bond content may be expected after prolonged treatment. However, such effect does not influence significantly the total fluorine content on the surface in the investigated range. Possibly, excessive exposure may cause significant modification and/or degradation of the chemical properties of the polymer as a consequence of the cleavage of the Si–C bonds; it is not excluded that if the exposure time is significantly increased this process may propagate from the surface to the bulk. Such phenomenon may be accelerated by the presence of defects on the surface; this, possibly, precludes the observation of a direct relationship between exposure time and the number of Si–F bonds which are formed.

Transferring CF_4 -Plasma-Etched Sample Topology onto Nonfluorinated Surfaces. Each plasma-treated sample was subsequently used as a template to replicate its topology by a double replica molding process. Figure 6 shows the scheme of the method we used. First, we cast the mixture of liquid PDMS and its catalyst on the plasma-treated surface (c). The liquid prepolymer conforms to the shape of the master and replicates the features of the master with high fidelity. After solidification at 80 °C for 12 h, the PDMS layer was peeled off (d): the low surface free energy and elasticity of PDMS allowed the release from the master without damaging the master or itself. This resulted in a complementary (negative) topographic surface structure of the original template. A second replication with PDMS was then performed on the negative template in the same manner as the first process (f). Before the replication, an antisticking treatment was performed to generate a release agent layer onto the negative template surface, and then PDMS was cured at 140 °C for 15 min this time. We obtained the antisticking layer by means of a very soft CF_4 -plasma treatment (20 sccm CF_4 flow, 100 mTorr pressure, 25 W power, 30 s exposure time) that

generated a thin Teflon-like antisticking layer on the PDMS surface but, as experimentally confirmed by AFM measurements, did not affect its topography. In this way, the complex surface patterns of CF_4 -plasma-etched samples (b) were transferred onto the surface of untreated PDMS samples with high fidelity (g). This fact was confirmed by AFM images analysis. We calculated the three most meaningful morphological parameters (root-mean-square roughness rms, peak-to-peak main value of the Gaussian distribution of asperity heights R_y , and autocorrelation length β^*) of the master CF_4 -plasma-treated samples and of their positive replicas for each exposure time. The results are reported in Figure 7.

The data show that samples having a surface covered by highly dense smaller protrusions were faithfully replicated and all the three parameter plots of both master and replica were substantially coincident. Nevertheless, for longer exposed samples, the fidelity of transferring was slightly reduced due to the bending of the highest and largely spaced hills during the first replication process (negative). Thus, for exposure durations longer than 40 min, the peak-to-peak mean height of replicated surface patterns was about 150–180 nm lower than the corresponding master surface value. Such differences can be however considered sufficiently narrow to allow us to compare the wettability properties of CF_4 -plasma-etched PDMS samples to those of their positive replicas by assuming they have the same topology.

As an example of pattern transfer fidelity, we report in Figure 8 the SEM images of a 30 min CF_4 -plasma-treated surface and its positive replica: as is clearly shown, the two samples exhibit the same morphology.

Moreover, to verify that the surface topography of our replicas was invariable when using the same template, we performed

Figure 6. Schematic illustration of the double replication process. Flat PDMS samples were exposed to CF_4 -plasma (a), and columnar-like structures topographies were obtained (b). A first replica molding process was performed (c and d), and a negative copy of the original topography was obtained (e). A second replica molding process (f and g) then allowed transfer of the topology of the fluorinated samples onto nonfluorinated ones.

several replications for each template, and all exhibited the same morphological features.

Subsequently, to investigate directly the singular effect of chemistry and topography on the wetting properties of CF_4 -

treated PDMS samples, we checked the chemical composition of each replicated surface by XPS analysis (an untreated PDMS sample was taken as reference) with the main issue being to demonstrate that they did not contain detectable fluorine traces

Figure 7. Comparison between the topology of CF₄-plasma-treated PDMS surfaces (filled dots) and the topology of their positive replicas (empty dots). Three main topological parameters were calculated by AFM image analysis: (a) Peak-to-peak mean value of the Gaussian distribution of asperity heights. (b) Autocorrelation length. (c) Root-mean-square roughness.

and that the fluorocarbon sputtered layer was not transferred onto the replicas' surfaces. This issue was confirmed by measurements.

Evaluating Roughness and Chemistry Roles in Enhancing PDMS Superhydrophobicity. Having determined a set of plasma

Figure 8. SEM images of the 30-min-plasma-treated PDMS master surface (a), of its negative replica (b), and of its positive one (c).

treatment conditions that allowed us to generate quasi-ordered columnar-like microstructures and being able to control their sizes within a wide range of values, we aimed to correlate the morphological characteristics and wettability of surfaces to investigate the singular effect of chemical and topological modifications on their wetting properties.

So, we compared the wettability properties of each CF₄-treated PDMS surface to those of its positive replica, with both surfaces having the same topology as it has been previously shown. In Figure 9, we report a plot of the measured static contact angle (CA) as function of rms roughness for a set of 10–80 min CF₄-plasma-“hard-treated” PDMS samples (all exhibiting a columnar-like structured morphology) and for their positive replicas.

As expected, the surfaces of the template samples showed remarkably higher CA values than the replicated surfaces. This has to be attributed to the presence of a Teflon-like surface layer deposited during CF₄-plasma treatment as previously discussed referring to XPS analysis.

In addition, remarkable enhancements in the hydrophobicity of the CF₄-plasma-treated PDMS samples were observed as treatment duration, and consequently surface roughness, increased. In particular, we found that the contact angle linearly

Figure 9. (a) Plot of static contact angle values of CF₄-plasma-treated PDMS samples and of their positive replicas as a function of roughness. (b and c) Direct observation of a 3 μ L water drop onto a 40-min-treated sample (b) and onto its positive replica (c).

Table 2. Comparison between Theoretically Predicted CA Values and Experimentally Measured Ones

CF ₄ -plasma exposure time (min)	autocorrelation length β^* (μ m)	Wenzel factor R_f	theoretical θ_w (deg)	Cassie–Baxter factor φ_s	theoretical θ_{CB} (deg)	measured $\theta_{\text{nonfluorinated}}$ (deg)	measured $\theta_{\text{fluorinated}}$ (deg)
10	0.67	1.31	119.4	0.785	120.6	121 $\pm$ 2	137 $\pm$ 2
20	1.09	1.68	128.9	0.602	128.6	126 $\pm$ 2	143 $\pm$ 2
30	1.42	1.88	134.6	0.494	133.7	135 $\pm$ 2	154 $\pm$ 2
40	1.76	1.93	136.2	0.422	137.4	140 $\pm$ 2	163 $\pm$ 2
50	2.17	2.13	142.9	0.401	138.5	145 $\pm$ 2	160 $\pm$ 2
60	2.55	2.20	145.6	0.380	139.7	146 $\pm$ 2	158 $\pm$ 2
70	2.91	2.35	151.9	0.295	144.6	148 $\pm$ 2	159 $\pm$ 2
80	3.02	2.51	160.6	0.248	147.7	150 $\pm$ 2	161 $\pm$ 2

increased up to the value of 163° observed for the 40 min-plasma-exposed sample that showed a 470 nm rms roughness and a 2.85 μ m peak-to-peak mean height of the hills. Similarly, the CA value of the nonfluorinated samples increased too. It was interesting to observe that the difference between the measured CA of fluorinated and nonfluorinated surfaces exhibited an almost constant value of $\Delta\theta \approx 20^\circ$ for topographies characterized by quasi-ordered columnar-like structures having an autocorrelation length up to 1.76 μ m and a peak-to-peak height up to 2.85 μ m.

This allows us to evaluate the effect of surface chemistry modification on the wettability properties of CF₄-plasma-treated PDMS samples. As shown from the data determined by XPS analysis in Table 1, the surface chemical composition remained almost constant when increasing treatment duration times and the atomic fluorine concentration was substantially the same for all samples. This means that the CA enhancement observed with increasing treatment duration time was solely due to increasing the quasi-ordered protrusion sizes, and hence, it is just related to the reduction of the interfacial tension as a consequence of the surface roughness rising. Whereas, the difference $\Delta\theta$ ($\approx 20^\circ$) in hydrophobicity observed between the master and replicated surfaces having the same topology was related to the fluorination of the former ones, and hence, it is related to the surface chemistry contribution.

No further increase of hydrophobicity was observed for fluorinated surfaces with bigger and largely spaced protrusions, but rather the CA remained almost constant for longer than 40 min CF₄-plasma-etched samples. On the contrary, the CA of nonfluorinated rough surfaces showed a raising trend, although with a lower slope, also for higher roughness values: a 150° CA value was found for the 80 min-like topology.

In other words, when the values of the autocorrelation length and peak-to-peak mean height became larger than a critical value ($\beta = 1.76 \mu\text{m}$, $R_y = 2.85 \mu\text{m}$), the CA difference between

fluorinated and nonfluorinated surfaces began to decrease. This is probably due to an intrinsic modification of the surface wetting behavior correlated to the presence of bigger and less dense hills; hence, a switch from a composite air–liquid–solid interface to a wetted one seems to occur for autocorrelation length values greater than 2 μ m.

Having separated chemistry and morphology effects, we compared the experimental measured CA values of eight replicated surfaces with those theoretically predicted by Wenzel and Cassie–Baxter. For this purpose, in Table 2, we compare the measured CA values of replicated surfaces ($\theta_{\text{nonfluorinated}}$) to those theoretically calculated by using the Wenzel (θ_w) and Cassie–Baxter (θ_{CB}) formulas for uncoated PDMS surfaces (by assuming $\theta_0 = 112^\circ$ for flat surfaces). We also reported in Table 2 the measured CA values of CF₄-plasma-treated PDMS samples ($\theta_{\text{fluorinated}}$); however, they are not to be compared to the Wenzel and Cassie–Baxter predicted ones because their actual θ_0 value is unknown. They should correspond in fact to the CA value of an hypothetical CF₄-plasma-treated flat PDMS surface. However, this value is not experimentally measurable because the surface chemistry of PDMS along with the surface morphology was changed after CF₄-plasma treatment.

For data points corresponding to autocorrelation length β^* values ranging from 0.67 μ m (10 min exposure time) to 1.76 μ m (40 min exposure time), we found that the measurements were closer to the angles predicted by the composite theory. This appears to be reasonable if one considers that the mean value of spacing between adjacent peaks is relatively low in these topographies if compared to longer exposed samples, and the protruding elements are extremely dense. It seems, in fact, that water drops probably did not penetrate valleys in the dense columnar-like microstructure forest giving rise to composite interfaces. On the contrary, when the autocorrelation length became larger than 2 μ m (data points from 50 to 80 min exposure

time), the drop began to wet also the cavities and the resulting surfaces showed a Wenzel-like behavior. Nevertheless, for the 80 min-like topology, the Wenzel theoretically predicted CA value was found to be dramatically higher than the experimental one. This is because the Wenzel roughness coefficient R_f assumed high values due to the large dimension of protrusions of such deep etched surfaces, but it does not take into account the texture design and the larger spacing between protrusions.

The transition from the Cassie to Wenzel regime also explains the reason why CF₄-plasma-treated samples with roughness values higher than 470 nm exhibited a practically constant CA value with slight oscillations between 158° and 161°.

In addition, we have to point out that the measured CA values of the replicated surfaces having $\beta^* = 1.42 \mu\text{m}$ and $\beta^* = 1.76 \mu\text{m}$ are almost coincident with both the Wenzel and Cassie–Baxter predicted ones; this means that their topographies well satisfy the design criterion for a robust superhydrophobic surface proposed by Patankar.³⁶ Indeed, a superhydrophobic surface is considered to be robust when there is minimal change in the apparent contact angle ($\theta_W \approx \theta_{CB}$) for a water droplet passing from a composite (Cassie–Baxter) to a wetted (Wenzel) contact. As shown from the data reported in Table 2, for such textured surfaces, the threshold value $\cos \theta_C$ between two regimes given by equating eqs 4 and 5 well satisfies the following equation:⁵⁰

$$\cos \theta_C \equiv \cos \theta_0 = \frac{\varphi_s - 1}{R_f - \varphi_s} \quad (8)$$

Referring to this criterion, we attested that nonfluorinated PDMS surfaces having topographies ranging from the 30 min-like one to the 40 min-like one exhibited stable superhydrophobic

behavior. So, we demonstrated a robust superhydrophobic surface fabricated by using a single-step large-scale technique such as CF₄-plasma treatment of PDMS. This fact is of fundamental importance to implement them on microfluidic applications in which undesired changes in wettability behavior should compromise device performance.

5. Conclusions

This study showed that CF₄-plasma treatment can be used as a versatile tool to create microstructured PDMS surfaces. In particular, by properly controlling plasma etching conditions, we were able to generate tailored surface topographies and tune their wetting properties up to obtain superhydrophobic surfaces. Besides, the superhydrophobicity of CF₄-plasma-etched surfaces can be attributed to the sum of two combined effects (roughness and fluorocarbon sputtered layer chemical hydrorepellence), of which each single influence was separated and studied. We found that, for highly dense columnar-like microstructures, the effect of a fluorinated layer covering surfaces produces an enhancement in the CA of about 20°. On the other hand, rough surfaces having largely spaced features (e.g., autocorrelation length larger than 1.76 μm) are less strongly affected by the chemical nature. At last, we have presented an easy and large-scale technique to create robust superhydrophobic surfaces for high throughput applications.

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