**Modification of poly(dimethylsiloxane) as a basis for surface wrinkle formation:
chemical and mechanical characterization**

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Abstract

In this manuscript, the processes occurring during UV-ozone treatment on polydimethylsiloxane (PDMS) surfaces i.e. formation of a stiff silica-like layer and surface degradation have been studied. While the chemical changes have been evaluated using Confocal Raman Microscopy (CRM) with submicrometer resolution, partial surface degradation occurring during longer ozone treatments have been evidenced both by Optical Profilometry and AFM.

Whereas previous studies reported the formation of a thin silica layer of around 20-30nm up to 200 nm depending on the method employed, herein, we demonstrated that in effect a thin rigid layer is formed but instead of a sharp interface predicted by previous reports a gradient depth profile was obtained. CRM evidenced the formation of a 4 μm layer of modified material. By Quantitative Nanomechanical Mapping (QNM) and based on the equations that predict the wrinkle formation, a surface layer thickness of around of 4.5 μm was also determined.

Keywords

UVO, surface modification, PDMS, surface mechanical properties, Confocal Raman, surface degradation, depth profile, Quantitative Nanomechanical Mapping

Introduction

Surface treatments of commodity polymeric materials are required in order to adapt them for a particular application. Most of the commonly used polymers are hydrophobic and for their final use several strategies of surface modification are nowadays available [1, 2]. In particular, polydimethylsiloxane (PDMS) is a widely used polymer for different applications including microfluidics [3] or for the fabrication of medical implants[4, 5] mainly due to its excellent

physical properties, low cost and ease of fabrication. Nevertheless, a major limitation for some applications concerns the intrinsic hydrophobic nature of the material. In order to increase the surface wettability, several approaches including oxygen or air plasma [6, 7], chemical modifications [8] or upon exposure to ultraviolet ozone (UVO) have been reported so far [9]. The surface treatments of PDMS have been employed for many different purposes. For instance, PDMS largely employed for the preparation of microfluidic devices has been functionalized to fabricate hydrophilic microfluidic channels [10]. Equally, changes on the interfacial PDMS chemical composition has been also carried out to enhance the adhesion properties with other interfaces [11]. Finally, the hydrophilic surface groups at the PDMS surfaces have been employed as support to fabricate polyelectrolyte multilayers by using layer-by-layer deposition techniques [6, 12]. Surface modification, is also essential in the formation of wrinkled interfaces. Wrinkling/buckling is one of the most extended strategies to prepare structured surfaces based on instabilities. Extensive experimental [13-17], and theoretical studies [18-22] have explored multifunctional micro/nano-scale surface patterns by harnessing spontaneous buckling of bilayer composite systems composed of a wide range of hard and soft materials.[13-16] Wrinkled interfaces prepared on elastic foundations exhibit potential interest for multiple applications [23, 24]: as templates [13-17], as platforms for flexible electronics [18-20], as supports with controlled/responsive wettability [21, 22] and/or adhesion [25-27] or for biorelated applications [28-30].

Independently of the strategies employed, wrinkled interfaces on elastic foundations require a composite system based on a homogeneous and uniform rigid thin layer. Different approaches have been employed to produce stiff films on stressed soft substrates including thermal plasma oxidation or UVO treatments or coating the surface with either polymers[31] or metals[32, 33]. Provided control over the thickness, tunable structural, mechanical, thermal, wetting and swelling properties can be varied.[24] As a result, control over the experimental parameters such as pre-stretching (direction, % of pre-strain, heating temperature) as well as film thickness or mechanical mismatch between the rigid layer and the soft foundation permitted the preparation of wrinkled

surfaces with variable amplitude and wavelength as well as wrinkle orientation. One of the most extended approaches to prepare wrinkles resort to the use of UVO treatments. The interaction of ozone (O_3) with PDMS produces the oxidation of the surface and thus the formation of a rigid silica-like layer. Some authors use extended treatment times that can go beyond two hours without taken into account whether degradation of the material could occur. In those studies they assumed a contraction of the directly exposed area and formation of a rigid layer of few nanometers that was evaluated by ellipsometry.[34] Nevertheless, the reports devoted to the oxidation process including depth profile analysis defined by the extent to which O_3 can penetrate into the PDMS bulk and attack the surface are still controversial. As a matter of fact, the depth of the treatment and/or the eventual degradation of the PDMS surface are aspects that have provided different results. Several studies including the work of Efimenko et al.[35] reported thicknesses of the rigid layer in the 60-80 nm range for exposure times ranging between 60 to 90 minutes respectively. On the contrary, Ouyang and coworkers [34] stated the formation of a thin skin of SiO_x with less than 20-30 nm thickness as determined by ellipsometry and XPS. Finally, Hillborg et al. [36] found an oxidized surface layer with a thickness of 130–160 nm using Neutron reflectometry and X-ray photoelectron spectroscopy. Only recently, Fery et al. [37] have tackled the problem of the non homogeneity of the rigid layer in the vertical direction, observing a depth gradient in the Young modulus.

In this work, we proposed the use of complementary techniques in order to unambiguously asses the UVO treatment effects on PDMS. In particular, two main aspects have been considered: 1) the depth of the attacked region and 2) the mechanical properties of the ozone exposed region. In this respect, we have first established the experimental conditions to produce the variation of the surface chemical composition. Secondly, we have analyzed the variations of the surface chemical by Confocal Raman Microscopy that allowed us, in addition, to analyze the depth of the treatment. Finally, Quantitative Nanomechanical Mapping (QNM) has been used in order to provide values for the elastic modulus of the treated region. Moreover, we will show that these values can be

employed to indirectly analyze the extent in depth of the modification by taking advantage of the wrinkle formation.

Results and discussion

A) Analysis of the PDMS surface modification

The chemical effect of ozone on PDMS has been studied by different research groups employing different techniques such as X-ray Photon Spectroscopy (XPS), Fourier Transform Infrared Spectroscopy (FTIR) or Atomic Force Microscopy (AFM) just to mention few of them.[38] These results indicated that, upon exposure to ozone, the methyl groups are replaced by silanol groups. As a result, the silanol groups that are polar in nature, transform the hydrophobic surface into a highly hydrophilic one. As depicted in **Figure 1(a)**, this can be observed by a dramatic change in the static contact angle of deionized water. Thus, surfaces exposed to UVO gradually decreased the contact angle during the first 40 minutes. An increase of the exposure to UVO produced a dramatic decrease up to 90 minutes. Larger exposures appeared to produce highly hydrophilic surfaces with contact angle values of around 30° or below (see Figure 1 (b)).

Figure 1. (a) Static water contact angle onto PDMS surfaces exposed to UVO at different times: 0 minutes, 10 minutes, 60 minutes and 120 minutes. (b) Evolution of the contact angle upon UVO treatments from 0 to 120 minutes. (c) Variation of the FTIR-ATR spectra upon exposure to UVO at different irradiation times ranging from 0 up to 120 minutes. (d) Evolution of the relative intensity between the bands at 1018 cm⁻¹ and 796 cm⁻¹ as a function of the irradiation time.

In addition, in this work the variation of the chemical composition of the PDMS surface during the UV-ozone treatment and the eventual interfacial degradation were investigated by micro-FTIR-ATR as well as Confocal Raman Microscopy, which will allow us to precisely understand the processes occurring at the interface. The oxidation of PDMS by UV/ozone treatments have been already explored and analyzed using FT-IR. [35, 39, 40] However, only recently Özçam et al [41] reported an exhaustive assignment of the FT-IR spectra required to understand the UV-ozone effect on the PDMS. As it is shown in **Figure 1(c)**, four main bands can be observed in the range between 700 and 1300 cm^{-1} in the FTIR-ATR spectra of the surface of PDMS irradiated samples. The first band at 785-815 cm^{-1} due to the $-\text{CH}_3$ rocking and asymmetric $\text{Si}-\text{C}\equiv$ stretching in $\text{Si}-\text{CH}_3$ decreased in intensity during the UVO irradiation. The same decrease was observed for the band at 1245-1270 cm^{-1} due to the symmetric $\equiv\text{Si}-\text{C}$ deformation in $\text{Si}-\text{CH}_3$ groups. Finally, two other bands centered at 1018 cm^{-1} and 1075 cm^{-1} exhibit contrary behaviors. The band at 1075 cm^{-1} due to the asymmetric $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ stretching and to the in-phase and out-of-phase wagging vibrations of $-(\text{CH}_2)-$ in $\equiv\text{Si}-(\text{CH}_2)_2-\text{Si}\equiv$ and in $\equiv\text{Si}-\text{CH}_2-\text{Si}\equiv$ decreases slightly during the UVO irradiation. On the other hand, the band at 1018 cm^{-1} due to the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ stretching increased during the formation of the rigid silica-like top layer. These results are in good agreement with previous reports [35, 39, 41] that found that all bands corresponding to methyl groups at 1245-1270 cm^{-1} and 785-815 cm^{-1} decreased rapidly in intensity at short irradiation times and more slowly for longer times due to the formation of a crosslinked layer formed by $\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}$ bonds. On the contrary, the bands characteristics of the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds at 1018 and 1075 cm^{-1} increases in intensity due to the formation of a rigid silica-like layer. From the infrared spectra taken at different UVO irradiation times it is possible to calculate the relative intensity of the 1018 and 796 cm^{-1} bands and thereby study the kinetic of the oxidation process of PDMS (**Figure 1-d**). More precisely, the ration between the maximum of the peak at 1018 cm^{-1} corresponding to the formation of the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds, divided by the maximum at 796 cm^{-1} resulting from the formation of $\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}$ crosslinking allowed us to follow the oxidation kinetics for the different exposure times. As can be seen, after the first 10 minutes, the methyl groups are replaced by $\text{Si}-\text{O}-\text{Si}$ bonds at a constant rate until 90 minutes. For longer treatments times it seems that

there is no change. These results exhibit a similar trend as the contact angle data presented in **Figure 1-b**.

In order to obtain contrasted information about the functionalization process, we covered the PDMS surface with a square-shaped mask during the UVO treatment. That enabled us to selectively produce exposed square areas in which the UVO oxidation took place, surrounded by areas protected by the mask during UVO treatment. Thus chemical analysis of the surfaces was performed recording spectra inside and outside the exposed areas. This study was carried out by Confocal Raman Microscopy. This technique provides better spatial resolution of about 300 nm in all three axes, in comparison with the 100 micros achieved in the micro-FTIR-ATR.

Figure 2(a) depicts the Raman spectra taken in the protected and the exposed areas during 60 minutes to UV/ozone. In the spectrum of the irradiated square there are two new bands at 753 and 936 cm^{-1} that do not appear in the protected one. So far these bands remain unassigned but most probably they can be associated to the formation of a rigid silica-like layer on the top surface. Moreover, in **Figure 2(b,c)** it is possible to observe that the relative intensity between the bands at 688 cm^{-1} and 709 cm^{-1} increased exclusively in the exposed squares as a function of the irradiation time while this relation did not change in the non-exposed areas. The first of these bands is assigned to Si-CH₃ symmetric rocking and the second to Si-C symmetric stretching [42, 43]. Besides in the exposed areas the band appearing at 491 cm^{-1} shifts to higher wavenumbers (up to 493.5 cm^{-1}) and broadens when increases the irradiation time while remains unchanged in the protected ones (**Figure 2-a**). This band is assigned to Si-O-Si skeletal deformation [44] and Si-O-Si symmetric stretching modes[40, 42, 43]. Equally, the band at 709 cm^{-1} in the exposed areas slightly shifts to lower wavenumbers when the UVO treatment duration increases.

As a result, the extent of the surface modification can be followed using any of the above mentioned Raman bands. For instance, the **Figure 2(c)** shows the variation of the relative intensity between the 688 cm^{-1} and 709 cm^{-1} bands as a function of the exposure time taking spectra inside and outside the oxidized square areas. An increase of the relative intensity occurs gradually by

increasing the duration of the treatment up to 90 minutes in which a plateau can be observed. This phenomenon could be explained assuming a complete conversion of the surface chemical groups into silica-like layer that may have been accomplished upon 90 min. This kinetic is similar to that discussed above to the infrared analysis and agrees with the contact angle data. However, neither this analysis nor previous reports taking into account that eventual partial degradation of the surface could also occur. On the contrary, previous reports assumed that UVO treatments involve a volume reduction during the formation of SiO_x . In order to assess this issue, the next series of experiments were conducted to elucidate the presence or not of degradation as well as the role of this process on the surface mechanical properties.

Figure 2. (a) Comparison of the Raman spectra obtained in exposed and protected areas upon treatment during 60 minutes and optical image of the selectively treated surface. (b) Evolution of the surface Raman spectra in exposed areas as a function of the exposure time. (c) Relative intensity of the bands at 688 cm^{-1} and 709 cm^{-1} for different irradiation times.

B) Mechanical properties of the UVO treated surface

In addition to the chemical changes at the surface, the mechanical properties upon UVO treatment have been evaluated by Quantitative Nanomechanical Mapping (QNM) using Atomic Force Microscopy (AFM).[45] For that purpose, the mechanical properties have been tested on the surface of samples irradiated using a mask to produce surfaces with a pattern of square treated areas surrounded by non-treated areas. Besides the topography of the sample (see **Figure 3(a)**), typical force-distance curves obtained are observed in **Figure 3(b)**. QNM technique therefore, allows obtaining maps of the variation of different mechanical magnitudes with spatial resolution on selectively treated samples. In our case, these magnitudes are related to the thickness of the rigid layer formed. **Figure 3(a)** shows the map of elastic modulus (central panel) and deformation (right panel) of a surface selectively treated by UV-ozone during 90 min. The measurements were obtained simultaneously with the topography presented in **Figure 3(a)** (left panel). As observed in the central panel of **Figure 3(a)**, UV-ozone treatment increases the stiffness of the PDMS, as indicated by the higher elastic modulus of this region. For the particular sample shown in **Figure 3(a)**, an average elastic modulus of around 50 MPa in the treated regions is obtained. However, in the regions protected with the mask during treatment, a value of elastic modulus $\sim 3\text{-}4$ MPa, was observed, which correspond to the values of the PDMS precursors, i.e. around ten times smaller. Both values are in good agreement with the average value reported by Fery *et al.*[37] for a similar polymer processed under similar conditions. Here it should be pointed out that in [37], QNM measurements were performed on cryotomed samples to obtain the Young modulus along the depth of the treated area, whereas in the present case, the measurements were performed indenting the top of the rigid layer. Fery *et al* found that the modulus gradually decreased from 120MPa in the outer region to finally reach the value of the untreated PDMS: In the present case a thin rigid layers rests on a soft layer of PDMS, and, due to the geometry of the measurement, this may provoke the observation of an average modulus value. Concomitantly, under the same peak force, 4pN in these experiments, the treated regions are less deformed. As observed in the right panel of **Figure 3(a)** a deformation of about 50 nm can be measured in those areas that have

been protected from UVO treatment. On the contrary, the deformation measured in the exposed areas decreases to close to 0 nm probing that a rigid surface layer was formed (right panel of Figure 3(a)).

The effect of O_3 treatment time was also studied by PF-QNM. **Figure 3(c)** shows how the mechanical magnitudes measured by PF-QNM vary with the time length of the UVO treatment. Measurements of the Modulus and of the Deformation were performed over the area of the treated region, precisely, $40\mu\text{m}$ images were taken at 204 lines and 204 points per line. The treated area has a dimension of about 19×19 microns. That gives an approximate number of 9500 measurements. The values presented in figure 3.c correspond to the average of these measurements. As observed, the modulus exhibits a maximum around 90 min of treatment. In the same way, the deformation of the treated regions decreases with time and it reaches a minimum at 90 min of treatment, indicating that the treated regions becomes more and more rigid as the UVO treatment is longer.

Figure 3.(a) QNM topography image (left), elastic modulus (center) and deformation (right) of a PDMS sample treated by UV-ozone during 90 minutes. (b) Force-distance (Z) curves: in the oxidized region, marked with 1 in the topography image, and in the protected areas, marked with 2 (approaching the sample surface has been labeled as trace and withdrawal as retrace). (c) Elastic Modulus and deformation measured inside the oxidized square areas as a function of UVO treatment time. Continuous lines are just eye guides.

C) Evaluation of the surface topography modification occurring during UVO treatment

The UVO treatment of PDMS surfaces has associated, as depicted above, significant changes on the chemical composition and the mechanical properties of the interfaces but also on a surface topography modification. As a result, in addition to chemical and mechanical variations, the duration of the exposure to O₃ is bounded with degradation processes occurring simultaneously. The optical profilometry analysis of the surfaces obtained upon UVO treatments are depicted in **Figure 4**. As can be clearly observed, already after 10 minutes of exposure the PDMS surface, in addition to the change the chemical surface composition discussed before, an erosion of the treated region takes place. This erosion is even more evident after 30 minutes and increases for longer treatments. The erosion of the PDMS can be also clearly seen in the cross-sectional profiles. These profiles indicated that the degradation of height occurring in the exposed areas produces a depth step that ranged from 70-80 nm after 10 minutes up to 300 nm after 120 minutes. These results were corroborated also by AFM, where a step between the untreated and treated regions could be observed (see Figure 3 (a)).

Figure 4. Left: 3D profilometry images of PDMS surface treated at different times using square pattern mask. Right: Cross-sectional profiles of the UVO exposed surface upon different irradiation times.

D) Estimation of the thickness of the functionalized layer

Another unresolved and controversial issue is the estimation of the thickness of the rigid layer formed upon UVO treatment. As mentioned in the Introduction, several authors have suggested that the thickness of the rigid layer for long treatments, estimated by ellipsometry and XPS, is below 100 nm [34, 35]. Herein, we employed two different approaches to estimate the thickness of the modified surface areas. On the one hand, confocal Raman Microscopy allowed us to analyze the variation of the chemical and structural features of the PDMS from the surface to the bulk. On the other hand, based on the theoretical equations for wrinkle formation we will be able to calculate the theoretical thickness of the rigid layer by inducing the formation of buckled surfaces and estimating its amplitude and period.

On one hand, depth profiling Raman maps of 0.5 μm large and 6 μm depth were recorded in the square irradiated areas of the samples treated at different times. The spectra were taken every 100 nm on a range of 1.5 μm above the PDMS surface and 4.5 μm below the surface at 3 seconds integration time using a 25 μm diameter pinhole to guarantee both the lateral and depth resolution better than 300 nm. From the analysis of the different features of the spectrum recorded at each point it is possible to construct different Raman maps. For example, the left top panel of the **Figure 5** shows the depth profiling map of the area of the Si-O-Si skeletal deformation band of PDMS at 491 cm^{-1} . However, an important issue that requires consideration is to precisely determine the Z-position of the PDMS-air interface. For that purpose, we integrated the area of the elastic scattering laser signal. This signal is associated to the laser light reflected from the sample without losing energy and is maximal at the interface between two different media having different refractive index, in our case air and oxidized PDMS. By taking into account this consideration we can fix exactly the Z-position of the surface and evaluate the variation of any spectral feature of the PDMS at different depths from the surface to the bulk.

For example, the central panel of **Figure 5** shows the depth profiling maps of the Raman shift at 491 cm^{-1} of the samples irradiated at different times. The profiles in **Figure 5-b** indicated that the maximum Raman shift was obtained at the surface of the samples. Analyzing other spectral parameters such as the relative intensity of the Raman bands at 688 and 709 cm^{-1} , the Raman shift of the 709 cm^{-1} band or the intensity at 753 cm^{-1} , it is always possible to conclude that the maximum value of the chemical transformation is obtained at the surface of the sample. In addition, it was observed that these maximum chemical transformations at the surface increased with the exposure time to the UVO treatment until it reached its maximum value at 90 minutes. It is very interesting that for treatments longer than 90 minutes the surface was not further oxidized. However, the thickness of the degraded upper zone was bigger than that of the 90 minutes sample (**Figure 5(b)**). Moreover, and more important is the fact that, as can be seen in **Figure 5(b)**, the Raman profiles indicated that the chemical transformation of the PDMS slowly decrease from the surface toward the inner bulk. At a certain depth the spectra are identical to

those observed in protected areas. The results depicted in **Figure 5** indicated that the depth affected increases gradually from few nanometers up to 4.5 μm for longer treatments (90-120 minutes). In fact, the sample exposed to O_3 during 10 minutes exhibits a modified layer of less than 2 μm . For the sample exposed 30 minutes, the layer thickness increases up to 3-4 μm whereas for longer irradiation times layer thicknesses above 4.5 μm were observed since the spectra measured at this depth indicated a partial oxidation. This result *a priori* contradicts previous reports[34, 41] that depicted the surface treatment depth on the nanometer scale. However, when analyzing the methodologies employed previously such as XPS, our results share common features. According to our findings we observed the formation of a thicker layer in which the UVO treatment has influenced. However rather than a sharp rigid layer we observed a gradual variation of the composition. Interestingly, the report of Ouyang et al. determine the thickness of the rigid layer based on stoichiometry close to that of SiO_2 that was only found at the outmost surface (~20-30 nm). However, they assumed a thin silica rigid layer but their report do not considered the effects of penetration of the O_3 below 20-30 nm. Our Confocal Raman Microscopy experiments also evidenced the formation of a more extensively reacted layer (depicted in yellow in **Figure 5(a)**) with submicrometer thickness upon 90 and 120 minutes that could agree with the observations of Ouyang et al. More interestingly, we evidenced that the O_3 further penetrates inside the bulk and oxidizes further below the surface to a lower extent up to 4-5 μm .

Figure 5.Top: Depth profiling Raman images of: Left: area of the 491 cm^{-1} band. Center: Raman shift of 491 cm^{-1} band of the samples irradiated at different times ranging from 10 to 120 minutes. Right: Depth profiles from the Raman shift images of the central panel. **Down:** Left: color scale bar to the area of the 491 cm^{-1} band. Right: color scale bar to the Raman shift of the 491 cm^{-1} band.

E) Estimation of the thickness of the functionalized layer by wrinkle formation

In order to obtain additional evidence about the depth of the PDMS affected layer, we took advantage of the wrinkle formation mechanism on PDMS films. As it has been widely described in the literature,[15] it is possible to form wrinkles on the PDMS upon pre-stretching prior to the UVO irradiation to create a rigid layer and subsequent stress relaxation. The wrinkle parameters including amplitude and period are directly related to both the extent of pre-stretching and the thickness of the rigid layer formed because of the oxidation during the UVO irradiation. Buckling of rigid thin layers attached to a compliant substrate upon compression is a very extended method to create topological patterns at the nano- and micrometer scale[24]. Under compression, buckling instabilities are caused by the mechanical mismatch between the thin stiff layer and the elastic substrate. In special cases this instability leads to wrinkle formation perpendicular to the strain

direction. If the strengths are small enough, the wavelengths of the resulting wrinkled pattern can be calculated from the well-known equations[32, 46]:

$$\lambda = 2\pi h_F \left(\frac{E_F}{3E_S} \right)^{1/3} \quad (1)$$

$$A = h_F \left(\frac{\epsilon}{\epsilon_c} - 1 \right)^{1/2} \quad (2)$$

$$\epsilon_c = -\frac{1}{4} \left(\frac{3E_S}{E_F} \right)^{2/3} \quad (3)$$

Where E_F and E_S are the elastic modulus of the film and the substrate respectively, h_F is the film thickness, ϵ is the applied strain and ϵ_c is the critical strain for buckling to occur. Equations 1-3 are obtained assuming $h_F \ll h_S$ where h_S is the compliant substrate thickness.

Since the elastic modulus for different oxidation times (E_F) was estimated by QNM, equation (1) could be used to obtain the thickness of the oxidized layer. For that purpose, wrinkled surfaces were prepared as follows. PDMS samples were pre-stretched at given strains and exposed to UVO irradiation while stretched for given times. After finishing the UVO exposure, the strain was released. This has the effect of applying a compression deformation on the newly formed rigid layer. For example, **Figure 6** shows the optical image of the wrinkled surface obtained in a sample pre-stretched at 20% strain, and UVO exposed for 120 min. As observed, strains of around 20% are necessary to appreciate wrinkles in these conditions. The profiles of such surfaces are obtained by optical profilometry and are shown also in **Figure 6**. The obtained profiles show that simple periodicity is only obtained for the sample pre-stretched at 20%, which shows a wavelength (λ) of around 43 microns. Higher strains produced non-linear effects like period doubling and even cracking. Using equations 1-3, and the values of the elastic modulus of both components obtained by QNM, $E_F = 31$ MPa and $E_S = 3$ MPa, and the wavelength observed by profilometry $\lambda = 43$ μm , a thickness of 4.5 μm is obtained. This result agrees with our estimations by Confocal Raman Microscopy. Using also these parameters, a value for the critical buckling strain ϵ_c of 11% can be obtained, explaining why no wrinkles are observed for the sample pre-stretched at 10%.

Figure 6: a) Optical image of a sample oxidized under 20% of strain. b) Surface profiles obtained by optical profilometry on 10% and 20% strained samples. The profiles have been vertically shifted for the sake of clarity.

Conclusions

In this manuscript we have analyzed the competitive processes taking place during UV-ozone treatment on PDMS surfaces. On the one hand, long ozone treatments lead to partial surface degradation and volume reduction. Surface treatments exceeding 30 min. involves not only the surface modification but also the erosion of the surface with variable depths ranging from 70-80 nm after only 10 min up to 300 nm upon 120 min. Interestingly enough, we further investigated the depth profile of the PDMS surface modification. Previous approaches indicated the formation of a thin silica layer of around 20-30 nm up to 200 nm depending on the method employed. Herein,

we demonstrated that a thin rigid layer is formed indeed but, instead of a sharp interface predicted by previous reports, a gradient depth profile was obtained. Confocal Raman Microscopy evidenced the formation of a 4 μm layer of progressively modified PDMS. More interestingly, we took advantage of the equations that predict the wrinkle formation in order to evaluate the thickness of the rigid layer. As a result, the periods observed of around 43 μm upon 20% pre-stretching also confirmed indirectly the formation of a surface layer of around of 4.5 μm . In contrast to previous methods employed to characterize this process such as ellipsometry or neutron scattering that require the knowledge of physical parameters (refractive index) or the use of complex simulations (for a gradient surface), Confocal Raman Microscopy allowed us to precisely determine in a direct manner with submicrometer resolution the effects of the UVO treatment inside of the PDMS, proving that there is a micrometer layer of modified PDMS below nanometer SiO_x layer, that it must be taken into account to explain the final physicochemical and mechanical properties of the UVO treated surfaces.

Experimental section

Characterization

Water contact angles (CA) were measured using a KSV Theta goniometer. The volume of the droplets was controlled to be about 2.0 μL and a charge coupled device camera was used to capture the images of the water droplets for the determination of the contact angles. Contact angle measurements were carried out in different films obtained at different irradiation time from 0 up to 120 minutes.

Micro-FTIR-ATR: Infrared spectra were recorded in a PerkinElmer Spectrum 100 FT-IR Spectrometer coupled with a Spectrum Spotlight 200 FT-IR Microscope. Spectra were taken in Total Attenuated Reflectance Mode using a germanium microcrystal probe of 100x100 microns with 4 cm^{-1} of spectral resolution and 20 scans.

Confocal Raman Microscopy: Raman spectra and images were recorded in a Confocal Raman Microscopy WITec Alpha 300 RA (Ulm, Germany) using a Nd:YAG laser of 532 nm wavelength

at 10 mW output power, through a 100X objective (N.A: 0.95) and two different gratings of 600 and 1800 grooves/line. The Raman images were taken point by point with each 100 nm with a piezodriven stage and an optical fiber of 25 microns in diameter as pinhole to guarantee a spatial resolution less than 300 nm. The software Witec Project Plus was employed to analyze the spectra and to make all the calculations and to build the Raman images.

Optical Profilometry: Analysis of the wrinkle formation as well as the cross-sectional profiles were obtained by using a Zeta-20 optical profiler (Zeta Instruments) with different optical objectives and with 13 nm of vertical resolution.

Quantitative Nanomechanical Mapping: AFM measurements were carried out in a Bruker Multimode 8, with a Nanoscope V controller, by the Quantitative Nanomechanical Mapping (PF-QNM) method. Measurements were performed at ambient conditions, using a standard cantilever holder. The quantitative measurements were carried out with MPP-2110–10 probes (Bruker). The actual cantilever spring constant (k , nominally 1–6 N/m), was measured by the thermal tune method and found to be around 2–3 N/m. Tip radius was calibrated against a polystyrene standard. In the PF-QNM method, quantitative values of the elastic modulus and deformation are obtained through force-distance curves that are collected by nanoindentation of the sample in a point-by-point fashion.[45] The maximum force (peak force) is controlled at each pixel to obtain force-distance curves which are then used as feedback signal.

Sample preparation

The PDMS pre-polymer was cured using a mixture 10:1 silicon oligomer to catalyst and placed in an oven at 65°C during 24h. The PDMS employed, Sylgard 184 is a mixture of different components provided in two parts, i.e. a base (Sylgard 184A) and a curing agent (Sylgard 184B). As has been recently described, the base contains vinyl-terminated PDMS oligomers 30–40wt% dimethyl vinylated and trimethylated silica, 1–5wt% tetra(trimethoxysiloxy)silane) and Pt based catalyst. The curing agent is a mixture of poly-(dimethyl-methylhydrogensiloxane) as the cross-linking agent (40–70wt%), vinyl-terminated poly(dimethylsiloxane) oligomers (15–40wt%), 10–

30wt% dimethylvinylated and trimethylated silica and 1–5wt% tetramethyl tetravinylcyclotetrasiloxane [40].

The cured PDMS samples were covered with copper-grids with variable sizes as masks and treated to UVO at different times from 10 min up to 120 min. For this study we employed two different square shaped masks having pitches of 25 and 12.5 μm .

Wrinkled formation

The generation of microwinkled surfaces has been carried out applying UVO treatment to a pre-stretched PDMS film. The UVO occurs using a low-pressure mercury lamp that emits at two different wavelengths, i.e., 185 and 254nm. The process generates simultaneously atomic oxygen when molecular oxygen is dissociated by 185 nm and ozone by 254 nm ultraviolet wavelengths. The 254 nm UV radiation is absorbed by most hydrocarbons and also by ozone. Therefore, when both UV wavelengths are present atomic oxygen is continuously generated, and ozone is continually formed and destroyed. As a result, using a UVO both near atomically clean surfaces can be achieved in minutes but also can be applied to chemically modify the surface of polymeric materials. All the crosslinked PDMS films were cut into 1 cmx5cm pieces and exposed to a uniaxial stretching of $\varepsilon=20\%$. The films were mounted into a home-made device to fix the film extremity permitting to apply the desired mechanical deformation.

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