Title: Use of statistical design of experiments in the optimization of Ar-O_2 low-pressure plasma treatment conditions of polydimethylsiloxane (PDMS) for increasing polarity and adhesion, and inhibiting hydrophobic recovery

Author: María Isabel Butrón-García José Antonio Jofre-Reche José Miguel Martín-Martínez

PII: S0169-4332(15)00169-5
DOI: http://dx.doi.org/doi:10.1016/j.apsusc.2015.01.144
Reference: APSUSC 29581

To appear in: *APSUSC*

Received date: 18-11-2014
Revised date: 18-1-2015
Accepted date: 19-1-2015

Please cite this article as: M.I. Butrón-García, J.A. Jofre-Reche, J.M. Martín-Martínez, Use of statistical design of experiments in the optimization of Ar-O_2 low-pressure plasma treatment conditions of polydimethylsiloxane (PDMS) for increasing polarity and adhesion, and inhibiting hydrophobic recovery, *Applied Surface Science* (2015), http://dx.doi.org/10.1016/j.apsusc.2015.01.144

HIGHLIGHTS

Design of experiments is effective in optimizing the LPP treatment conditions of PDMS

Working pressure in LPP treatment affects markedly the hydrophobic recovery (ageing) of PDMS

Low power and long duration of LPP treatment retard ageing

Use of Ar + O_2 mixtures for LPP treatment of PDMS is more efficient than Ar or O_2 only

Surface modifications of LPP treated PDMS under optimal conditions are maintained for 14 days

Use of statistical design of experiments in the optimization of Ar-O_2 low-pressure plasma treatment conditions of polydimethylsiloxane (PDMS) for increasing polarity and adhesion, and inhibiting hydrophobic recovery

María Isabel Butrón-García, José Antonio Jofre-Reche and
José Miguel Martín-Martínez*

Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain

---

* Corresponding author. Tel.: +34 965903977 ; Fax: +34 965909416;
E-mail adress: jm.martin@ua.es

Abstract

Polydimethylsiloxane (PDMS) film was treated with RF low-pressure plasmas (LPPs) made of mixtures of oxygen and argon for increasing surface polarity, minimizing hydrophobic recovery (i.e. retard ageing) and increasing adhesion to acrylic adhesive tape for medical use. Statistical design of experiments has been used for determining the most influencing experimental parameters of the LPP treatment of PDMS. Water contact angle values (measured 24 hours after treatment) and the O/C ratio obtained from XPS experiments were used as response variables. Working pressure was the most influencing parameter in LPP treatment of PDMS, and the duration of the treatment, the power and the oxygen-argon mixture composition determined noticeably its effectiveness. The optimal surface properties in PDMS and inhibited hydrophobic recovery were achieved by treatment with 93vol% oxygen+7vol% argon LLP at low working pressure (300 mTorr), low power (25 W) and long duration of treatment (120 seconds).

Keywords: PDMS, low-pressure plasma, surface treatment, hydrophobic recovery, ageing, water contact angle, XPS, adhesion.

1. Introduction

PDMS is biocompatible amorphous polymer [1,2] commonly used in medical devices including contact lenses, denture liners, wound dressing, drug delivery systems, catheters, ear correctors and implants. The particular properties of PDMS derived from its chemical structure made of siloxane (Si-O) backbone with methyl pendant groups and its higher ionic character derived from the higher electronegativity of oxygen and the lower electronegativity of silicon with respect to that of carbon. As a consequence, PDMS is more polar and stable than other polymers (i.e. the silicon-oxygen bond energy is higher than for carbon-carbon bonds [3]) which justify its high thermal stability, chemical inertness, and flexibility. However, the non-polar nature of the methyl pendant groups in PDMS structure results in low intermolecular forces and internal mobility imparting high hydrophobicity. Because of its hydrophobicity, PDMS shows low wettability and low surface energy, and its adhesion is also poor.

In some medical devices made in PDMS (catheters or ear correctors for example), polarity is mandatory and it must last over time. Plasma treatments have been used often for increasing the polarity of the PDMS surface, and the effects produced have been widely studied in the past. Although different mechanisms for explaining the modification of PDMS produced by plasma treatment have been proposed, it is commonly accepted that bond scission and oxidation of methyl groups in the polymeric chains of PDMS are the most relevant [4-5] and they produced the formation of a silica-like layer on the PDMS surface; as a consequence, an increase in the surface energy and hydrophilicity of PDMS is produced, and the formation of micro-cracks on the brittle silica-like layer surface too [6-10]. However, the migration of low molecular weight species from the bulk to the PDMS surface across those cracks and the reorientation of the new polar groups towards the bulk produced the loss of the hydrophilicity with time after plasma treatment, causing fast ageing (i.e. hydrophobic recovery) in 24 hours after treatment [11-14].

The influence of the plasma treatment conditions on the surface modifications of PDMS and their stability have been studied extensively [6,13-21]. It has been demonstrated that the extent of ageing or hydrophobic recovery depended on the experimental parameters of the plasma treatment including its duration [15-18], power [6,18,19], composition of the gas used for generating the plasma

[13,14,16,18,20], working pressure [6,17], and extent of crosslinking of PDMS [21-22], among other. However, the influence of these parameters on the hydrophobic recovery of LPP treated PDMS have been studied separately.

Although the influence of the experimental conditions of the LPP treatment determined the adhesion and the extent of hydrophobic recovery in PDMS, a systematic study involving simultaneously all relevant experimental parameters has not been carried out up yet. A statistical design of experiments methodology was used in this study and all relevant experimental parameters in the LPP treatment of PDMS were varied simultaneously in order to find the optimal conditions for increasing the surface polarity and adhesion to acrylic tape, and minimizing at the same time its hydrophobic recovery, i.e. retard ageing. The seven most relevant experimental parameters of the LPP treatment of PDMS used in this study were the gas composition, the power, the duration, the working pressure, the distance between the power and the ground shelves, the distance between the PDMS surface and the plasma source, and the extent of crosslinking of PDMS. Once the optimal conditions were obtained, the LPP treated PDMS surface was characterized, and its adhesion to acrylic adhesive tape and the extent of hydrophobic recovery with time under storage in open air were studied too. Furthermore, different mixtures of argon and oxygen for LPP treatment of PDMS were used and these mixtures has not used in the existing literature yet.

2. Materials and methods

2.1. Materials

Two commercial room temperature moisture vulcanizing (RTV) polydimethylsiloxane prepolymers with different degree of crosslinking, Elastosil E-41 and Elastosil E-43 (Wacker Silicones AG, Munich, Germany) were used. These prepolymers were selected because their formulations allowed produce different degree of crosslinking when they are cured in presence of moisture at room temperature. PDMS films were prepared by placing a solution of 75 wt% prepolymer in methyl ethyl ketone (for reducing its viscosity) in a clean leveled Mylar® surface under reduced pressure (50 mTorr) during 1 hour for allowing solvent removal and avoid bubbles formation; afterwards, the film was cured under open air at 25ºC and 50% relative humidity for 3 days. Finally, the cured PDMS film of 1 mm thick was placed under reduced pressure (50 mTorr) during 10 hours for removing potential byproducts of the polymerization.

2.2. Low-pressure plasma (LPP) treatment

Low-pressure RF (13.56 MHz) plasma treatment of PDMS was carried out in capacitively coupled discharge NT-1 Supersystem equipment (BSET-EQ, Pittsburg, PA, USA) using different mixtures of oxygen and argon (99.999% purity; supplied by Abelló-Linde, Barcelona, Spain). The scheme of the plasma chamber used in this study is given in Figure 1. The PDMS film was placed on the floating shelf between the power and ground electrodes, the power electrode was placed above the PDMS surface. The experimental parameters of the LPP plasma treatment of PDMS studied simultaneously were the gas composition (G), the power (Pw), the duration (t), the working pressure (Pr), the distance between the power and the ground electrodes (d), the distance between the PDMS surface and the power electrode (h), and the extent of crosslinking of the PDMS (S).

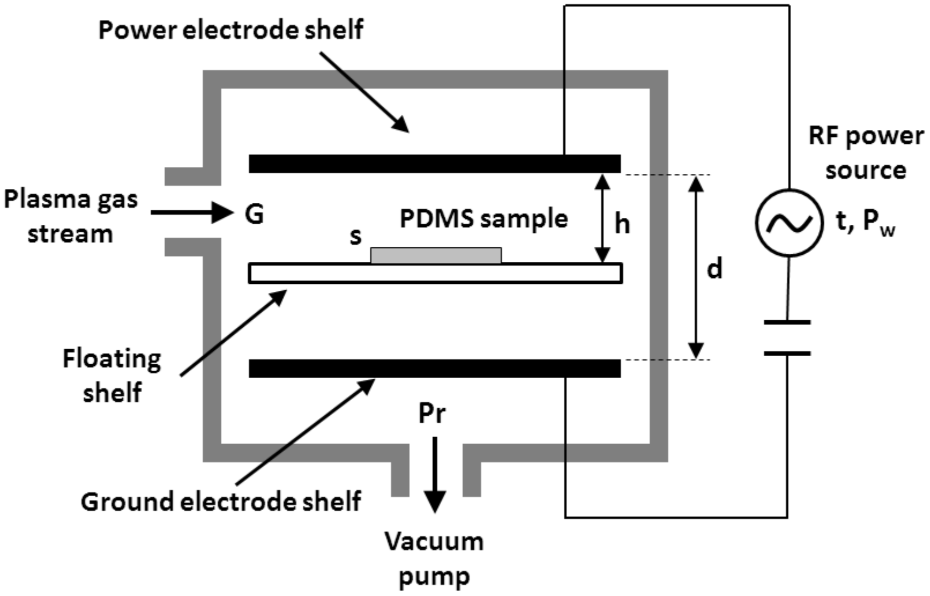


Figure 1. Low-pressure plasma chamber configuration used in this study.

2.3. Statistical design of experiments

Statistical experimental design methodology was used to identify the most influencing experimental parameters of the LPP treatment of PDMS which produce the optimal surface properties and the slowest ageing over time. Screening design based on Plackett-Burman matrix was selected and Doehlert experimental plan was chosen because of its spherical domain with uniformity in space filling, its ability to extend the results obtained for two-factors to three factors, its ability to explore the whole domain and its potential to reuse the experiment when the boundaries have not been well chosen initially [23].

2.4. Experimental techniques

Contact angle measurements. The changes on the wettability of the LPP-treated PDMS were assessed by measurements of the contact angle values at 25 ºC in ILMS 377 goniometer (GBX Instruments, Bourg de Péage, France). At least five drops of 4 µl of deionized bidistilled water (polar test liquid) or diiodomethane (non-polar test liquid) were placed on the LPP-treated PDMS surface and the contact angles were measured immediately and 24 hours after LPP plasma treatment on both sides of the drops and averaged.

The surface energy of the LPP treated PDMS was calculated following the Owens, Wendt, Rabelt and Kaeble approach - equation (1) :

$$1 + \cos\theta = \sqrt{\gamma_s^d}\left(\frac{\sqrt{\gamma_l^d}}{\gamma_l}\right) + 2\sqrt{\gamma_s^p}\left(\frac{\sqrt{\gamma_l^p}}{\gamma_l}\right) \qquad (1)$$

where θ is the contact angle, $\boldsymbol{\gamma_l}$ is the surface tension of the liquid and $\boldsymbol{\gamma_l^p}$ and $\boldsymbol{\gamma_l^d}$ are its polar and dispersive components respectively; $\boldsymbol{\gamma_s^p}$ and $\boldsymbol{\gamma_s^d}$ are the polar and dispersive components of the surface free energy of the PDMS respectively. The total surface energy of the LPP treated PDMS is obtained by adding the corresponding polar and dispersive components [24].

On the other hand, the stability of the surface modifications on the LPP treated PDMS (i.e. the extent of ageing or hydrophobic recovery) was monitored by measuring the water contact angle values measured 24 hours after treatment.

ATR-IR spectroscopy. The chemical composition of the LPP treated PDMS surfaces was analyzed by infrared spectroscopy in attenuated total reflectance (ATR) mode using Alpha IR spectrometer (Bruker Optiks GmbH, Etlingen, Germany) with Germanium prism. The incidence angle of the IR beam was 45º and 60 scans were recorded and averaged with a resolution of 4 cm^{-1}. Under these experimental conditions, the depth of the PDMS surface analyzed was about 1 μm.

X-ray photoelectron spectroscopy (XPS). The chemical modifications on the outermost untreated and LPP treated PDMS surfaces were assessed by XPS using K-Alpha Thermoscientific instrument (Thermo Fischer Scientific, Waltham MA, USA) provided with Al-Kα X-Ray source (1486.6 eV) and twin crystal monochromator, operating at 3 mA and 12 kV; the residual pressure during the experiments was lower than $2 \cdot 10^{-9}$ mTorr. Two XPS experiments on the same sample were carried out and the results were averaged with an error lower than 0.01 at%.

Scanning electron microscopy (SEM). The topography of the untreated and LPP treated PDMS surface was examined by SEM in Jeol JSM-840 microscope (JEOL Ltd., Tokyo, Japan). For improving contrast the surface of PDMS was gold coated, and the energy of the electron beam was 12 kV.

Atomic force microscopy (AFM). The nanoroughness on the untreated and LPP treated PDMS surface was analyzed by AFM in NTEGRA Prima microscope (NT-MDT, Moscow, Russia) in an area of 25x25 μm under semi-contact mode.

Adhesion measurement. Adhesion was obtained from T-peel tests of adhesive joints made with untreated and LPP treated PDMS and acrylic adhesive tape for medical use (3M Co., St. Paul, MN, USA). The dimensions of the PDMS samples were 20×50 mm. During joint formation pressure was applied manually by rolling ten times a cylindrical rod (25 mm width, 100 mm diameter) of 1 kg weight over the adhesive joints. The adhesion was measured 2 hours after joint formation in TA-TX2i Texture Analyzer equipment (Stable Micro Systems, Surrey, UK) by using a pulling rate of 1 mm/s.

3. Results and discussion

3.1. Survey screening in LPP treatment of PDMS

The most influencing experimental conditions of the LPP treatment favouring the increase in polarity and minimizing the hydrophobic recovery of PDMS were determined by using Plackett-Burman layout screening simultaneously seven process parameters or factors (Table 1) at two levels of values, i.e. the highest and the lowest values for each parameter. Table 1 shows the values of the seven experimental parameters of the LPP treatment of PDMS used in the survey screening, and they are the power supplied by the RF power source to ionize the gas (A), the duration of the LPP treatment (B), the working pressure in the plasma chamber (controlled by the flow rate of the inlet gases) (C), the composition of the gas – i.e. mixtures of oxygen and argon – in the plasma chamber (D), the degree of crosslinking of the PDMS (E), the distance between the PDMS surface and the power electrode (F), and the distance between the power and the ground electrodes (G). The range of values for the power, working pressure, duration of treatment and degree of crosslinking of PDMS were selected according to previous papers [6,13-22]; the range of values for the rest of parameters (i.e. the maximum and minimum positions of the floating shelf and the power electrode, and the distance between the power and the ground electrodes) were the maximum and minimum ranges in the plasma equipment.

The water contact angle (WCA) values measured immediately (WCA-0h) and 24 hours after treatment (WCA-24h) on the LPP treated PDMS surface were chosen as response variables in the statistical experimental design to evaluate the relative influence of each factor or experimental parameter. The percentage of hydrophobic recovery on the PDMS surface within 24 hours after LPP treatment was also used as response variable, and it was calculated as the relative increase in the water contact angle values measured immediately and 24 hours after LPP treatment.

Table 1. Experiments performed in Plackett-Burman layout screening design to find the most influencing experimental parameters in the LPP treatment of PDMS. WCA : Water contact angle.

Run	**A (W)**	**B (min)**	**C (mTorr)**	**D (%O_2-Ar)**	**E**	**F (cm)**	**G (cm)**	**WCA-0h (deg)**	**WCA-24h (deg)**
1	100	1	200	80-20	low	4.8	12.4	1±1	70±3
2	100	5	200	20-80	high	2.3	12.4	17±2	53±1
3	100	5	600	20-80	low	4.8	7.5	14±1	87±2
4	25	5	600	80-20	low	2.3	12.4	13±1	83±2
5	100	1	600	80-20	high	2.3	7.5	9±2	101±4
6	25	5	200	80-20	high	4.8	7.5	11±1	67±2
7	25	1	600	20-80	high	4.8	12.4	8±1	86±1
8	25	1	200	20-80	low	2.3	7.5	5±1	62±1

Table 2 shows the regression coefficients for each parameter obtained from the statistical analysis using the different response variables; positive or negative sign of the coefficients (β) indicates that the parameter value increases or decreases the corresponding response variable, respectively. According to Table 2, the wettability of the PDMS surface immediately after LPP treatment during 5 minutes is lower than during 1 minute (positive regression coefficient), likely due to overtreatment, in agreement with previous studies [17,18]; however, longer LPP treatment provides lower water contact angle values 24 hours after treatment and, in consequence, lower degree of hydrophobic recovery and higher ageing stability. A similar conclusion is obtained by varying the oxygen content in the gas composition of the plasma. On the other hand, the working pressure shows the highest positive coefficient value indicating that the higher is the working pressure, the higher is the water contact angle 24 hours after treatment and, therefore, the higher is the hydrophobic recovery.

Table 2. Regression coefficients values (β) of the factors obtained from the statistical analysis of the screening experimental design of LPP treated PDMS for each response variable. WCA: Water contact angle.

Response variable	β_A	β_B	β_C	β_D	β_E	β_F	β_G
WCA (0 h)	-0.2	4.0	1.5	-1.2	1.5	-1.2	0.2
WCA (24 h)	-3.1	-3.6	13.1	4.1	0.6	1.4	1.6
Percentage of hydrophobic recovery	-2.9	-7.6	11.6	5.4	-0.9	2.6	1.4

By using the regression coefficient values in Table 2, the relative influence of the different experimental parameters or factors was obtained and it was calculated as the percentage of variation for each factor on the response variable when it was varied between its corresponding low and high level value by keeping constant the rest of factors. Figure 2 shows the relative influence of each factor on the response variable (i.e. water contact angle values) for the LPP treatment of PDMS. The duration of the LPP plasma treatment is the most influencing factor (67%) on the wettability of the PDMS surface just after treatment, followed by the working pressure (9%) and the crosslinking degree of PDMS (9%). On the other hand, according to Table 1, the water contact angle value of the PDMS surface measured 24 hours after LPP treatment is higher than immediately after treatment, indicating that hydrophobic recovery is produced.

If the water contact angle value measured 24 hours after LPP treatment is used as response variable, the working pressure is the most influencing parameter (80%) (Figure 2), and the duration of treatment, the gas composition and the power are also relevant. On the other hand, although the degree of crosslinking of PDMS has a noticeable effect on the water contact angle value measured immediately after LPP treatment, it has not an influence on the water contact angle value measured 24 hours after LPP treatment. Furthermore, the distance between the PDMS surface and the power electrode has minor effect on wettability and hydrophobic recovery in the LPP treated PDMS. As the main objective of the study was retard ageing of the LPP treated PDMS surface, the most influencing parameters of the plasma treatment was selected by using the water contact angle values obtained 24 hours after plasma treatment (WCA-24h) as variable response.

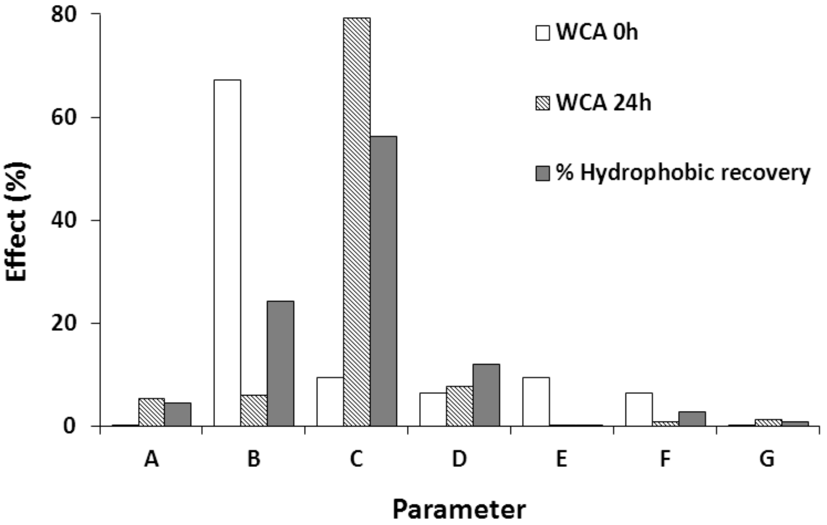


Figure 2. Relative influence of each parameter and percentage of hydrophobic recovery in LPP treated PDMS on the wettability measured immediately and 24 hours after treatment. WCA: Water contact angle.

3.2. Influence of the working pressure in the plasma chamber on the LPP treatment of PDMS

Since the most influencing experimental parameter of the LPP treatment of PDMS that inhibits more the hydrophobic recovery is the working pressure in the plasma chamber, the water contact angle values measured 24 hours after LPP treatment were measured by changing the working pressure and fixing the rest of the parameters at intermediate values; the potential mislead information obtained from these experiments is assumable as long as the effect of the working pressure is huge as compared to that of the rest of the experimental parameters in the LPP treatment (Figure 2).

Figure 3 shows the variation of the water contact angle values measured 24 hours after LPP treatment of PDMS as a function of the working pressure. For working pressure value below 300mTorr, the water contact angle value does not vary significantly and it is low, whereas fast hydrophobic recovery is produced for working pressure above 400mTorr. Therefore, the working pressure during LPP treatment should be 300 mTorr or lower for inhibiting hydrophobic recovery in the PDMS surface.

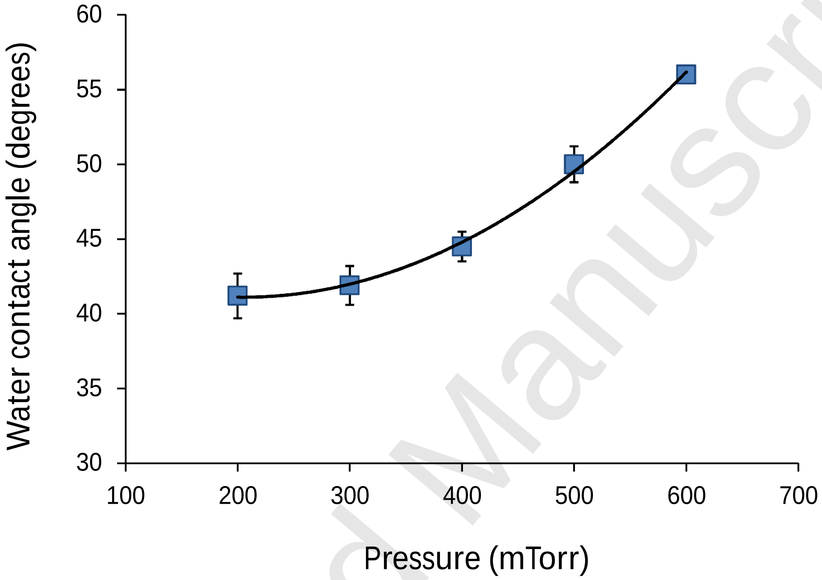


Figure 3. Variation of the water contact angle values measured 24 hours after treatment on LPP treated PDMS surface as a function of the working pressure in the plasma chamber.

3.3. Influence of the power and the duration of treatment on the effectiveness of the LPP treatment of PDMS

The working pressure was set at 300 mTorr and the influence of other most influencing experimental parameters (i.e. duration of treatment, gas composition and power) on the effectiveness of LPP treatment on the surface modifications of PDMS and their stability over time were studied simultaneously by using Doehlert experimental design (Figure 4). The domain limits of the experimental parameters were set to shorter ranges at lower levels or values of parameters, to ensure that the analysis is carried out in a region with marked effect of the factors and for enhancing the reliability of the Doehlert experimental design. Therefore, the duration of LPP treatment is varied between 30 and 150 seconds, and the values of power range between 10 and 50 watts. Later, the experimental points placed in the mid-plane of the spherical experimental domain, where the gas composition is constant (mixture of 50vol% Ar and 50vol% O_2) - Figure 4, right -, were analyzed to determine if the variations of the duration of treatment and the power are independent or not. The distance between the electrodes and the distance between the PDMS surface and the power electrode were fixed at 10 cm and 5 cm, respectively, and the PDMS with higher degree of crosslinking was used.

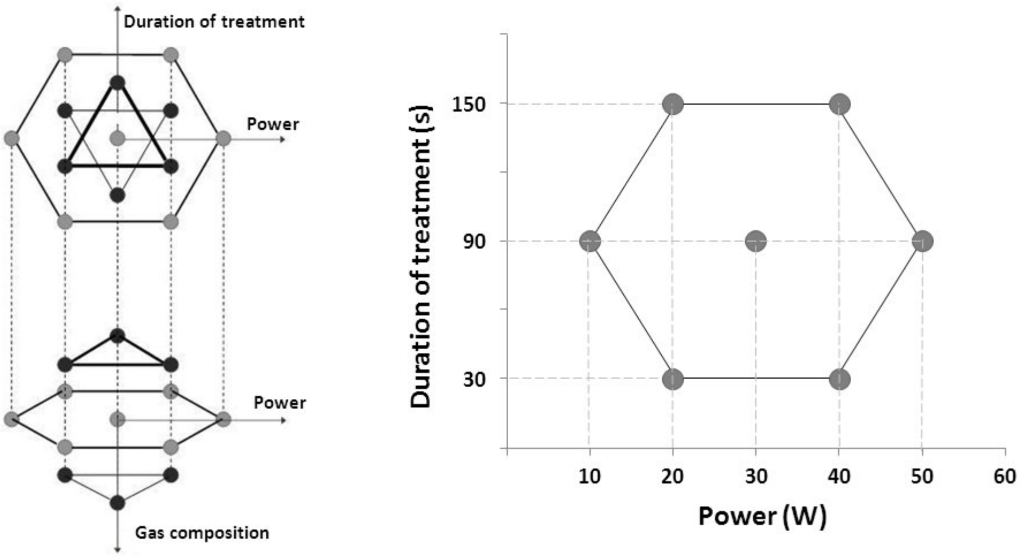


Figure 4. Doehlert experimental plan for LPP treatment of PDMS varying the duration of treatment, the power and the gas composition (left), and experimental domain of the mid-plane region showing the range of values chosen (right).

The surface energy of the LPP treated PDMS surface obtained from the contact angle values measured 24 hours after treatment was chosen as response variable for determining the optimal values of the duration of treatment and the power. The water (θ_w) and diiodomethane (θ_I) contact angle values on the untreated and LPP treated PDMS surface at different values of the duration of treatment and the power are shown in Table 3 in which the values of the polar, dispersive and total surface energy (γ^p, γ^d and γ^t, respectively) are also given.

Table 3. Values of contact angles and surface energies on untreated and LPP treated PDMS surface at different values of power and duration of treatment.

Time (s)	**Power (W)**	θ_w **(deg)**	θ_i **(deg)**	γ^p **(mJ/m^2)**	γ^d **(mJ/m^2)**	γ^t **(mJ/m^2)**
Untreated	Untreated	117±0	73±0	0	19.4	19.4
30	20	54±0	44±1	21.1	27.2	48.3
30	40	43±1	46±1	32.3	23.5	55.8
90	10	33±0	45±1	38.5	23.0	61.5
90	30	31±1	48±1	40.9	21.3	62.2
90	50	35±1	35±1	36.9	23.4	60.3
150	20	27±1	46±0	42.8	22.0	64.8
150	40	30±1	46±1	40.2	22.8	63.0

Figure 5a shows the dependence of the surface energy on the LPP treated PDMS surface (taken as response variable) on the duration of LPP treatment and the power, and Figure 5b shows the curve levels plot of iso-response. Both figures show that the highest surface energy values correspond to the LPP treatment of PDMS carried out for long time and low power. Moreover, the slope of the response surface plot in Figure 5a indicates that the influence of the duration of treatment is a more influencing parameter than the power, in agreement with the results shown in Figure 2. Furthermore, the changes in the slope along the response surface plot indicate the existence of an interaction between the duration of treatment and the power, i.e. the effect of the duration of treatment on the effectiveness of LPP treatment of PDMS surface depends on the value of the power or vice versa. In fact, the dependence of the duration of treatment and the power on the contact angle values has been shown previously [25,26]. On the other hand, the interaction between the duration of treatment and the power is also observed in Figure 6 in which the variation of the oxygen-carbon ratio obtained from XPS experiment as response variable ii used. According to Figure 6, as the two lines are not parallel, the effects of the power and the duration of treatment are not independent. Furthermore, according to Figure 5a, higher surface energies are obtained when short treatment and high power are used in the LPP treatment of PDMS and vice versa, but according to Figure 6 the higher oxygen-carbon ratio values correspond to the higher O/C values. The mislead information obtained from Figures 5a and 6 can be explained from the curve fitting (70% Lorentz – 30% Gauss mixed-model was used) of the Si2p$_{3/2}$ photopeaks of the LPP treated PDMS surfaces.

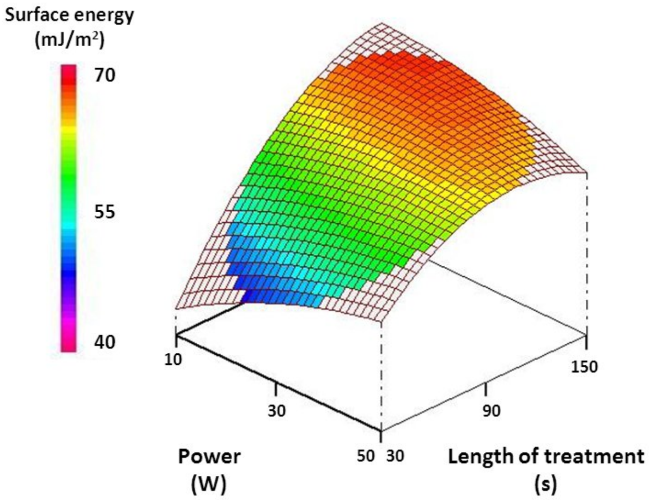


Figure 5a. Surface response plot of LPP treated PDMS surface for different values of duration of treatment and power. Surface energy is used as response variable.

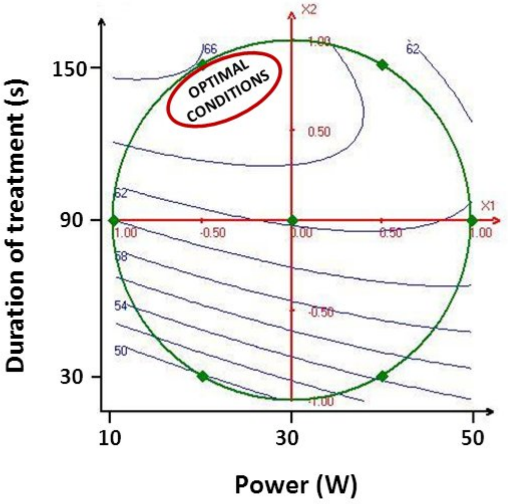


Figure 5b. Optimal values of power and duration of treatment for the LPP treatment of PDMS that maximizes the surface energy measured 24 hours after LPP treatment.

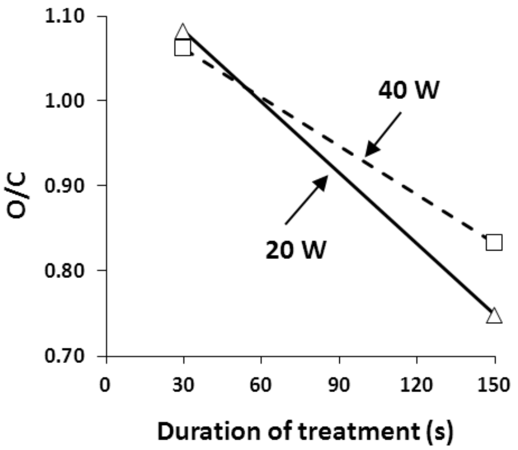


Figure 6. Variation of the oxygen-carbon (O/C) ratio obtained from XPS experiment as a function of the duration of the LPP treatment at different values of power.

Figure 7 shows the curve fitting of the $Si2p_{3/2}$ photopeaks of the LPP treated PDMS materials with different power and duration of treatment. Three contributions can be distinguished at binding energies of 102.1 eV, 102.8 eV and 103.4 eV corresponding to $SiO_2(CH_3)_2$, $SiO_3(CH_3)$ and SiO_4 species respectively [22,27]. Figure 7 and Table 4 show that the LPP treated PDMS surface with lower oxygen/carbon ratio (i.e. 20 W and 150 s) contains higher amount of SiO_4 species (silica-like layer) indicating that the LPP treatment using low power and long duration shows the smallest hydrophobic recovery, likely due to the crosslinking caused by the silica-like layer created on the surface which prevents the reorientation of the oxidized species towards the PDMS bulk and the migration of low molecular weight non-polar species from the bulk to the surface as well. However, in the LPP treated PDMS surfaces with higher O/C ratios, during hydrophobic recovery the oxygen species may have been moved a few monolayers under the outermost surface, and they can be detected by XPS but not by water contact angle measurements. Moreover, the O/C ratio may increases by rising the oxygen content on the LPP treated PDMS surface and/or by leaving off methyl groups. On the other hand, considering that the theoretical atomic content of silicon in as-received PDMS is quite similar to the experimental one obtained using XPS (Table 4), the O/Si ratio seems more reliable for analyzing the extent of hydrophobic recovery. In fact, the LPP treated PDMS surface with high power and long time shows a lower content of fully oxidized silicon species, i.e. SiO_4 species, which could be an indication of ablation.

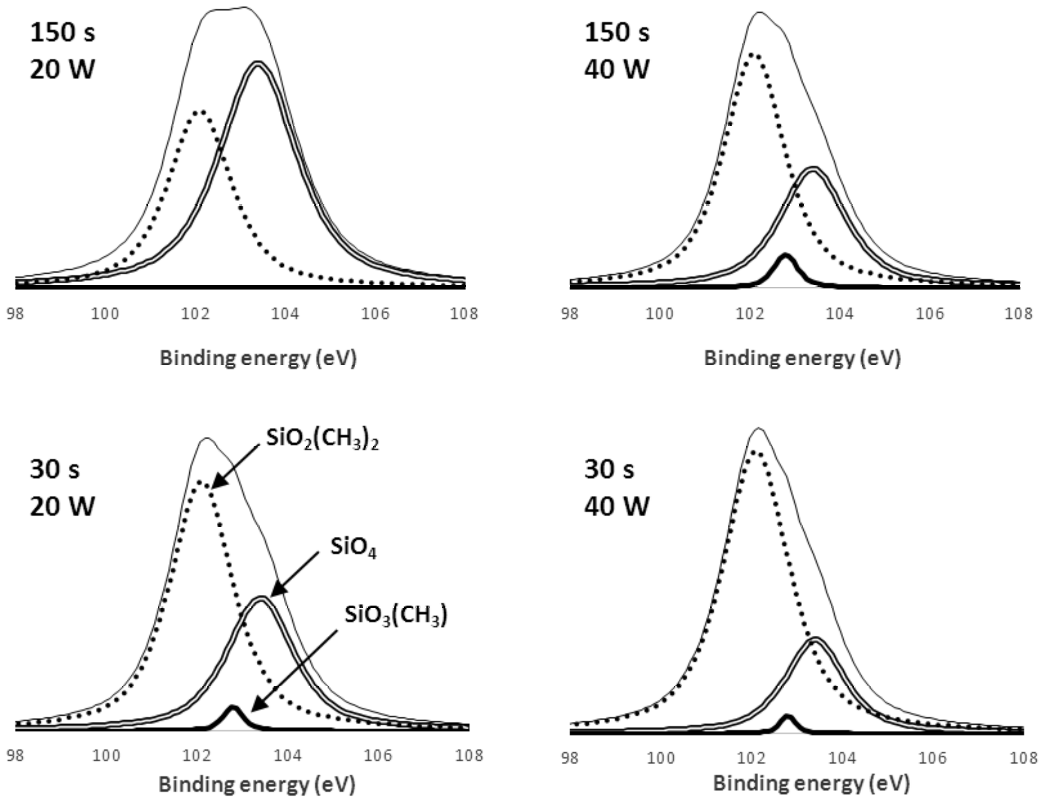


Figure 7. Curve fitting of $Si2p_{3/2}$ photopeaks on the LPP treated PDMS surfaces with different power and duration of treatment. XPS experiments.

Table 4. Atomic percentages of the species obtained from the curve fitting of $Si2p_{3/2}$ photopeaks of LPP treated PDMS surfaces, and O/C and O/Si ratios obtained from the survey XPS experiment.

Power (W)	**Time (s)**	**$(CH_3)_2SiO_2$ (at%)**	**CH_3SiO_3 (at%)**	**SiO_4 (at%)**	**O/C**	**O/Si**
20	30	62.7	1.9	35.4	1.1	1.9
20	150	38.8	0	61.2	0.8	2.7
40	30	62.0	3.5	34.5	1.1	1.6
40	150	76.3	1.1	22.6	0.8	1.4
Untreated	Untreated	88.3	0.0	11.7	0.5	1.4

3.4. Influence of the gas composition (argon + oxygen mixtures) on LPP treatment of PDMS

For analyzing the influence of the gas composition of the plasma on the surface modifications of PDMS and their stability over time, different mixtures of argon and oxygen were used; the power was set to 25 W and the duration of treatment was varied. The water contact angle values measured 24 hours after LPP treatment were used as response variable. Figure 8 shows the surface response of the water contact angle values on LPP treated PDMS surface as a function of the gas mixture composition and the duration of treatment. The treatment with plasmas enriched in oxygen produces more stable hydrophilic PDMS surfaces 24 hours after LPP treatment, whereas for the plasmas enriched in argon the more stable hydrophilic surfaces are obtained for lower duration of treatment (60–90 seconds); however, more hydrophobic PDMS surfaces 24 hours after treatment are obtained by increasing the duration of LPP treatment.

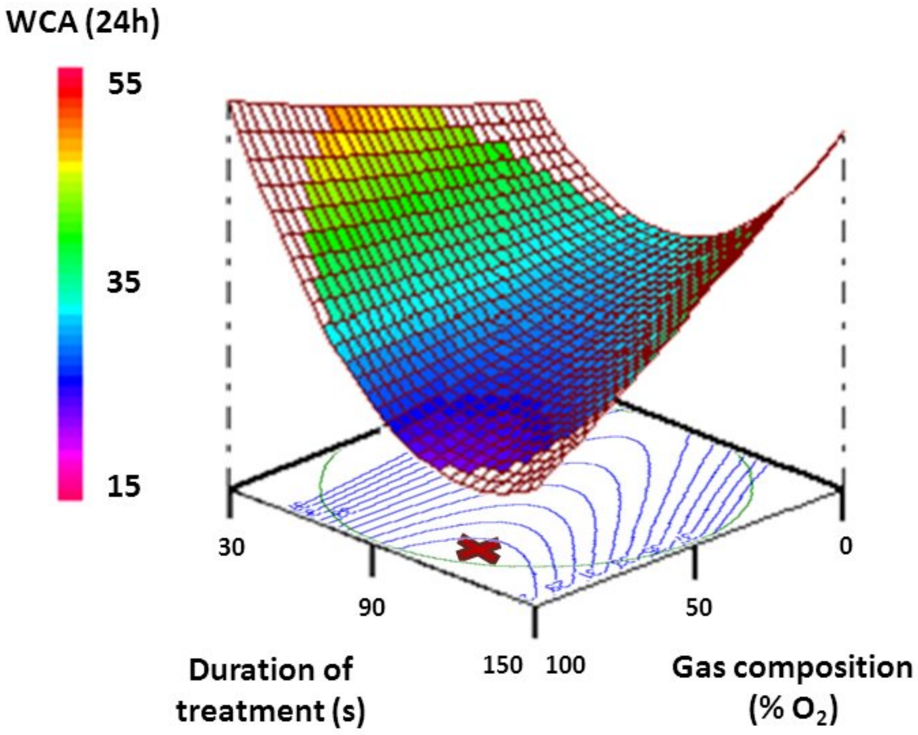


Figure 8. Surface response of the water contact angle values on LPP treated PDMS surface measured 24 hours after treatment as a function of the duration of treatment and the composition of the gas mixture.

The treatment of PDMS surface with oxygen-enriched plasmas creates higher amount of polar groups than with argon-enriched plasmas, and the most stable surface is obtained with the LPP treatment with 93vol% oxygen + 7vol% argon plasma during 120 seconds (Figure 8). This can be explained by considering that argon promotes the ionization of oxygen during plasma treatment due to the longer lifetime and higher energy of argon metastable excited atoms (lower ionization energy is required by argon than by oxygen [28,29]). On the other hand, due to excessive ion bombardment, overtreatment of the PDMS can be produced with argon-enriched LPP longer than 90 seconds, this may cause loss of hydrophilicity.

The chemical modifications produced on the PDMS surface treated with oxygen, argon and oxygen+argon low pressure plasmas with 25 W and 120 seconds were analyzed using ATR-IR spectroscopy. Under the experimental conditions used in this study, the depth of the PDMS surface analyzed by ATR-IR spectroscopy is about 1 μm. Figure 9a shows the ATR-IR spectra of the untreated and LPP treated PDMS surfaces in which the main absorption bands due to PDMS can be observed. The bands at 1082 and 1016 cm^{-1} correspond to simmetric and asimmetric stretching of siloxane (Si-O) respectively, the band at 1260 cm^{-1} corresponds to bending of $Si-CH_3$ and the band at 795 cm^{-1} corresponds to stretching of $Si-(CH_3)_2$ [30]. According to Figure 9a, the treatment with oxygen or argon plasmas increases slightly the intensity of the siloxane absorption bands with regard to these of the untreated PDMS indicating that if some chemical modifications are produced by treatment with plasma they must be located on the outermost surface; however, the treatment with 93vol% oxygen + 7vol% argon plasma produces an increase of the intensity of the siloxane band likely due to the creation of thicker silica-like layer due to deeper PDMS surface modification. The creation of the thicker silica-like layer is evidenced better in the $Si-O/Si-CH_3$ ratios given in Table 5 in which the highest values correspond to the 93vol% oxygen + 7vol% argon plasma treated PDMS. Moreover, Figure 9b shows a higher intensity of the broad OH band in the 3000-3600 cm^{-1} region of the ATR-IR spectra in the 93vol% oxygen + 7vol% argon LPP treated PDMS indicating that the formation of the crosslinked silica-like layer seems to be produced by hydroxilation of the silicon atoms.

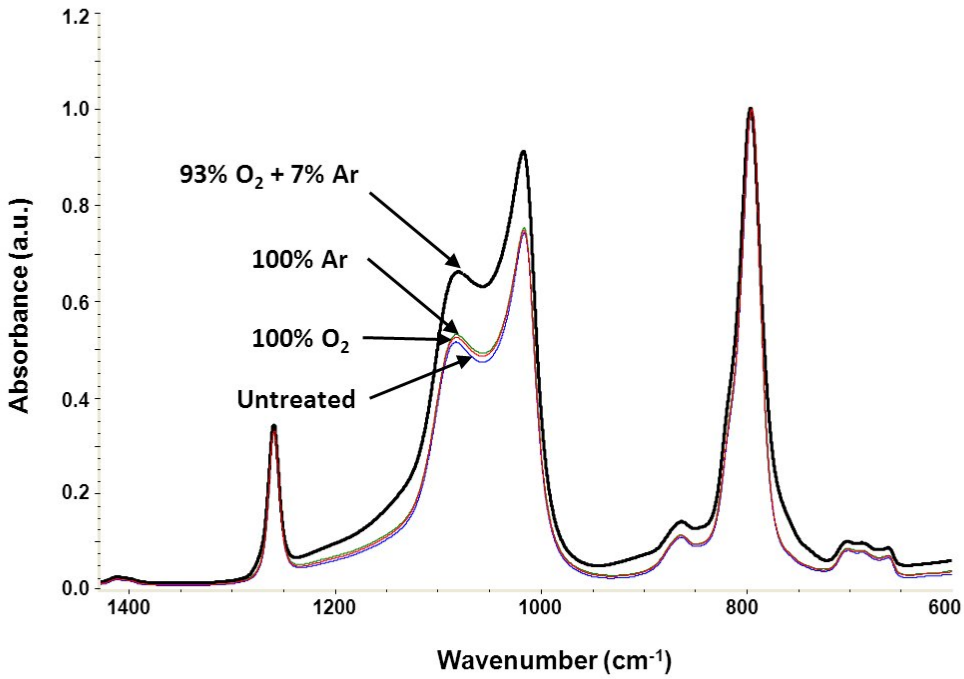


Figure 9a. ATR-IR spectra of the untreated and treated PDMS with LPP of different gases. Power: 25 W; duration of treatment: 120 s.

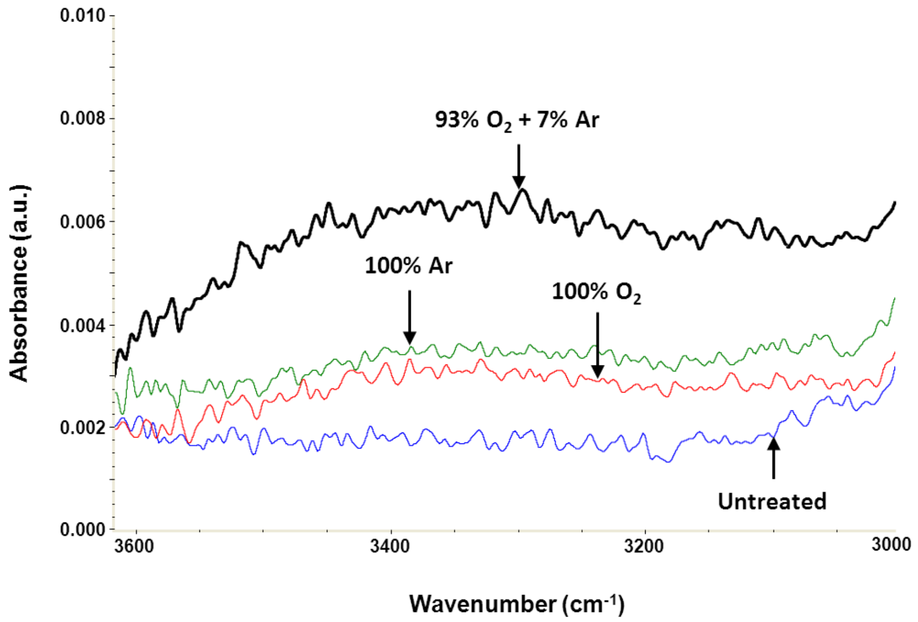


Figure 9b. Region of hydroxyl group vibrations in the ATR-IR spectra of untreated and treated PDMS with LPP of different gases. Power: 25 W; duration of treatment: 120 s.

Table 5. Ratio of the intensities of the bands of Si-O and Si-CH_3 (Si-O/Si-CH_3) in the ATR-IR spectra of the untreated and treated PDMS with LPP of different gases.

Gas composition (vol%O_2-vol%Ar)	**Si-O/Si-CH_3**
0-100	0.54
93-7	0.66
100-0	0.53
Untreated	0.52

The chemical composition on the outermost PDMS surface treated with oxygen, argon and 93vol% oxygen + 7vol% argon plasmas was obtained using XPS. The PDMS surface treated with argon plasma shows higher oxygen content than the one treated with oxygen gas and 93vol% oxygen + 7vol% argon mixture plasmas (Table 6); however, the curve fitting of the $Si2p_{3/2}$ photopeaks (Figure 10, Table 7) shows that the argon LPP treated PDMS surface has higher amount of non-oxidized $(CH_3)_2SiO_2$ species (38.9at%) than in the PDMS treated with oxygen (30.3at%) and the 93vol% oxygen + 7vol% argon (24.3at%) plasmas. The lower content of non-oxidized siloxane species in the 93vol% oxygen + 7vol% argon LPP treated PDMS is an indication of the existence of a thicker silica-like layer, in agreement with the higher intensity of the Si-O bands at 1082 and 1016 cm^{-1} and the more intense OH band at 3000-3600 cm^{-1} shown in the ATR-IR spectrum (Figures 9a and 9b).

Table 6. Chemical surface composition on untreated and treated PDMS surface with LPP of different gases. XPS experiments.

Gas composition (vol%O_2-vol%Ar)	**C (at%)**	**O (at%)**	**N (at%)**	**Si (at%)**	**O/C**	**O/Si**
0-100	32.5	42.3	0.3	24.9	1.3	1.7
93-7	**38.5**	**38.9**	**0.2**	**22.4**	**1.0**	**1.7**
100-0	38.0	38.4	0.0	23.6	1.0	1.6
Untreated	53.9	26.6	0.2	19.3	0.5	1.4

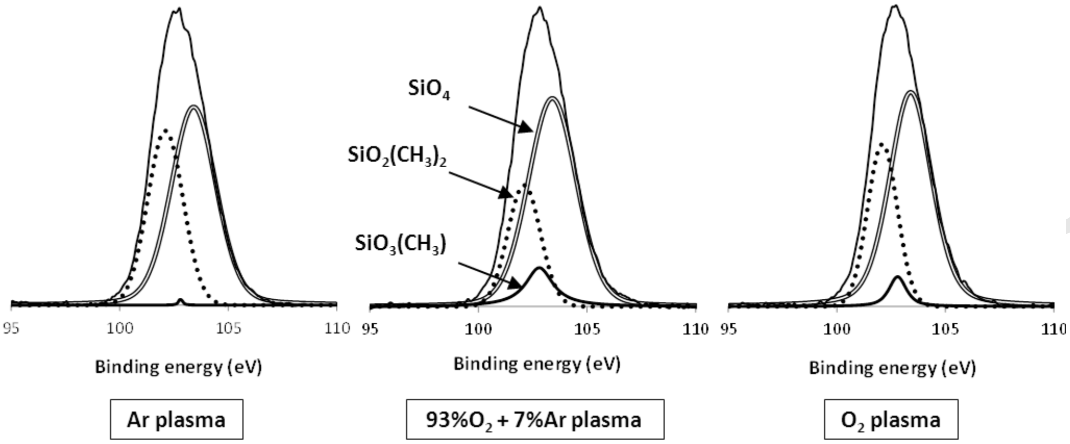


Figure 10. Curve fitting of the Si2p$_{3/2}$ photopeak on argon (a), 97vol% oxygen + 7vol% argon (b) and oxygen (c) LPP treated PDMS surface. XPS experiments.

Table 7. Atomic percentages of the species obtained from the curve fitting of the Si2p$_{3/2}$ photopeak of PDMS surface treated with LPP of different gases. XPS experiments.

Gas composition (vol%O$_2$-vol%Ar)	**(CH$_3$)$_2$SiO$_2$ (at%)**	**CH$_3$SiO$_3$ (at%)**	**SiO$_4$ (at%)**
0 – 100	38.9	0.2	60.9
93 – 7	**24.3**	**9.8**	**65.9**
100 - 0	30.3	4.3	65.4
Untreated	88.3	0.0	11.7

The extent of ablation produced on the PDMS surface by treatment with LPP of different gases can also be evaluated from the weight loss produced during treatment. The weight losses were referred to the surface area of each LPP treated PDMS (Table 8). The most noticeable weight loss corresponds to the argon LPP treated PDMS because important etching is produced. On the other hand, the treatment of PDMS with 93vol% oxygen + 7vol% argon LPP produces moderate etching but the degree of oxidation produced is important (according to the surface chemical composition given in Table 6).

Table 8. Weight losses in PDMS after LPP treatment with different gases.

Gas composition ($vol\%O_2$-$vol\%Ar$)	Weight loss per surface area (mg/cm^2)
0-100	0.050
93-7	0.040
100-0	0.035

The changes on the PDMS surface topography caused by treatment with 93vol% oxygen + 7vol% argon LPP with 25 W and 120 seconds were evaluated by SEM and AFM. SEM micrographs (Figure 11) shows the formation of some few cracks on the LPP treated PDMS surface due to the brittleness of the silica-like layer on its surface. Figure 12 shows the 2D amplitude and 3D AFM micrographs of the untreated and LPP treated PDMS surface. The ablation caused on the PDMS surface by treatment with 93vol% O_2 + 7vol% Ar plasma is observed and the presence of small thin nanocracks can also be distinguished. Because of the ablation produced, the average surface roughness value of the PDMS surface decreases from 33 nm (untreated) to 26 nm in the 93vol% O_2 + 7vol% Ar LPP treated PDMS, confirming the combined effect of oxidation and ablation produced by 93vol% oxygen + 7vol% argon plasma treatment.

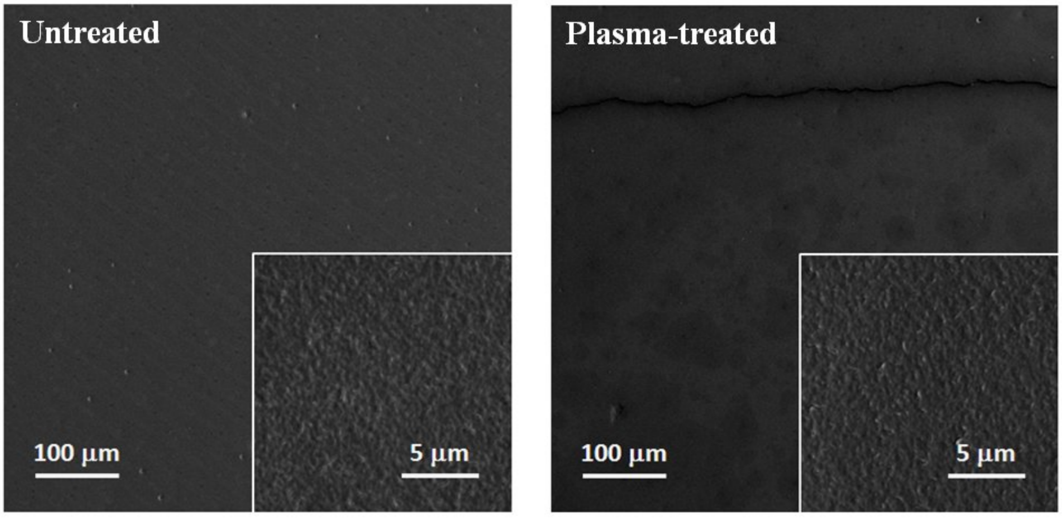


Figure 11. SEM micrographs of untreated and 93vol% O_2 + 7vol% Ar LPP treated PDMS surface with 25 W for 120 seconds.

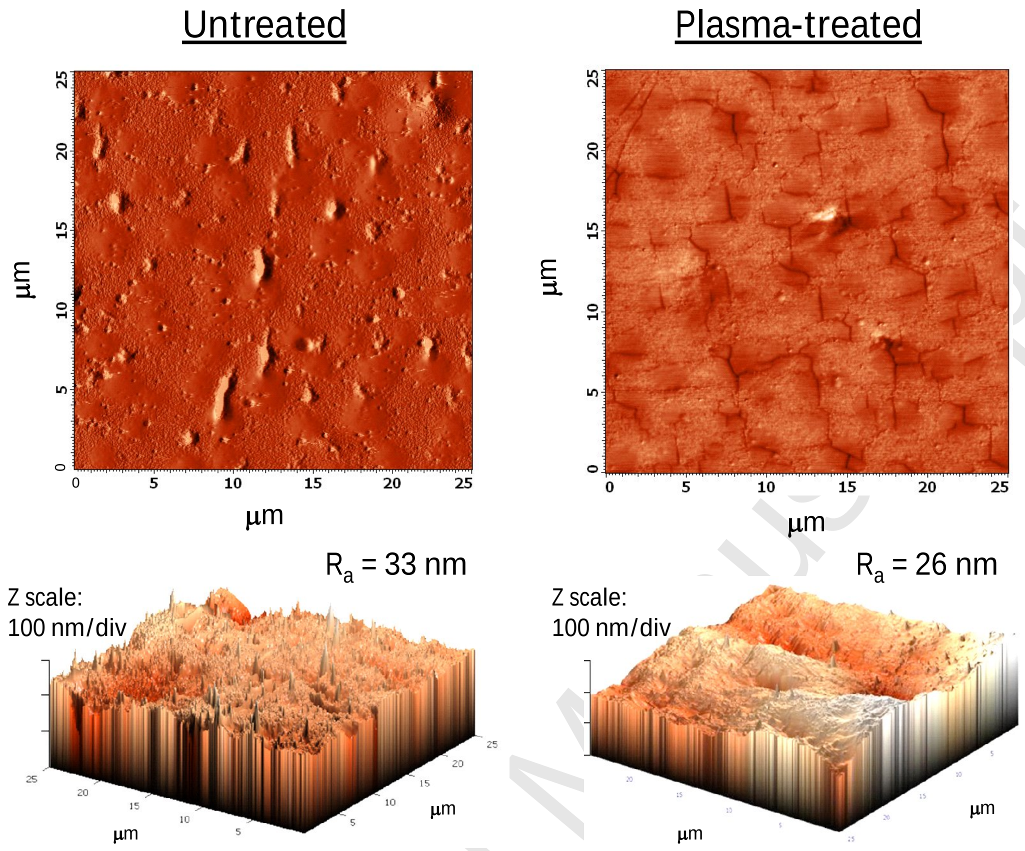


Figure 12. 2D amplitude (top) and 3D (down) AFM micrographs of untreated and 93vol% O_2 + 7vol% Ar LPP treated PDMS surface with 25 W for 120 seconds.

The effect of the LPP treatment with different oxygen and argon mixtures on the hydrophobic recovery of the PDMS surface was monitored by measuring the water contact angle values on the treated surfaces stored in open air for two weeks. Figure 13 shows a fast initial increase in water contact angle value up to 35 degrees during 12 hours after treatment in all LPP treated PDMS surfaces irrespective of the gas composition of the plasma. However, the rate of increase in water contact angle value, or in hydrophobic recovery, depends on the composition of the plasma for longer times after treatment. Thus, the oxygen LPP treated PDMS surface suffers faster hydrophobic recovery than the argon LPP treated one, although after seven days both reach similar water contact angle values. The hydrophobic recovery in the 93vol% O_2 + 7vol% Ar LPP treated PDMS is the slowest one and even 14 days after treatment the water contact angle value is 10 degrees lower than for the other LPP treated PDMS surfaces.

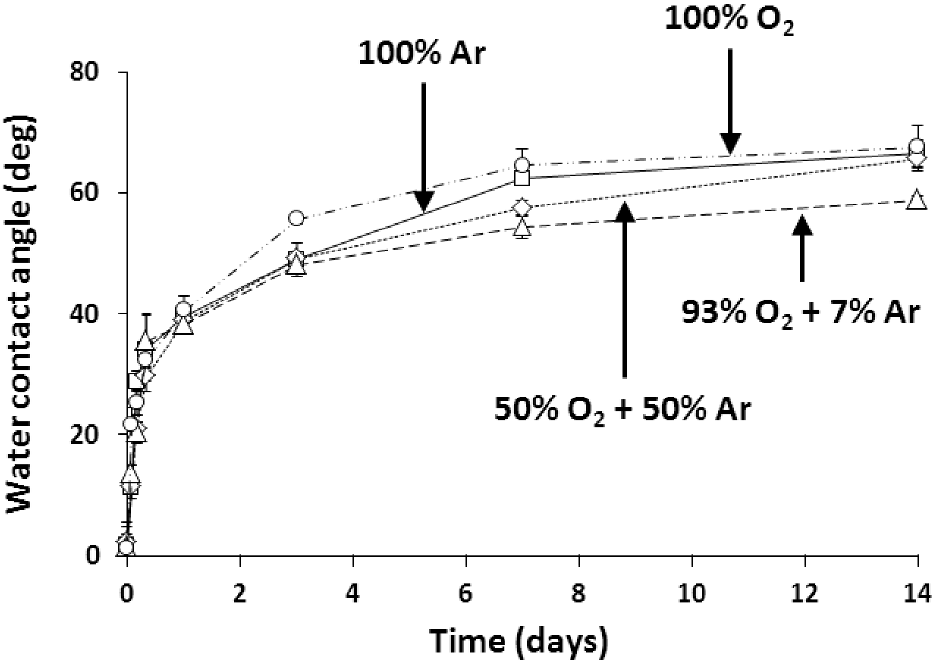


Figure 13. Variation of the water contact angle values (25ºC) on PDMS surface treated with oxygen, argon and different oxygen and argon mixtures LPP as a function of the time after treatment. 25W, 300mbar, 120s.

Hydrophobic recovery was also monitored by following the variation on the surface chemistry on the LPP treated PDMS surfaces. Table 9 shows the chemical composition on the PDMS surface treated with oxygen, argon and different oxygen and argon mixtures LPP measured 14 days after treatment. All LPP treatments show lower carbon and higher oxygen content than for the untreated PDMS, the highest O/C ratio corresponds to the treatment with 93vol% O_2 + 7vol% Ar LPP. Furthermore, the silicon content in all LPP treated surfaces is higher than for the untreated PDMS likely due to the creation of the silica-like layer.

Figure 14 shows the silicon species content obtained 14 days after treatment from the curve fitting of the $Si2p_{3/2}$ photopeaks of the untreated and oxygen, argon and different oxygen and argon mixtures LPP treated PDMS. All LPP treated PDMS surfaces show an important percentage of SiO_4 species, the highest one corresponds to the PDMS surface treated with 93vol% O_2 + 7vol% Ar LPP, confirming the inhibition of the hydrophobic recovery in PDMS by treatment under the optimal conditions derived from the statistical design of experiments.

Table 9. Chemical surface composition 14 days after treatment of untreated and oxygen, argon and different oxygen and argon mixtures LPP treated PDMS. XPS experiments.

Gas composition **(vol%O_2-vol%Ar)**	**C** **(at%)**	**O** **(at%)**	**N** **(at%)**	**Si** **(at%)**	**O/C**
0-100	42.0	37.3	0.0	20.7	0.9
50-50	38.0	39.3	0.2	22.5	1.0
93-7	**34.8**	**42.3**	**0.2**	**22.7**	**1.2**
100-0	38.3	38.2	0.0	23.5	1.0
Untreated	53.9	26.6	0.2	19.3	0.5

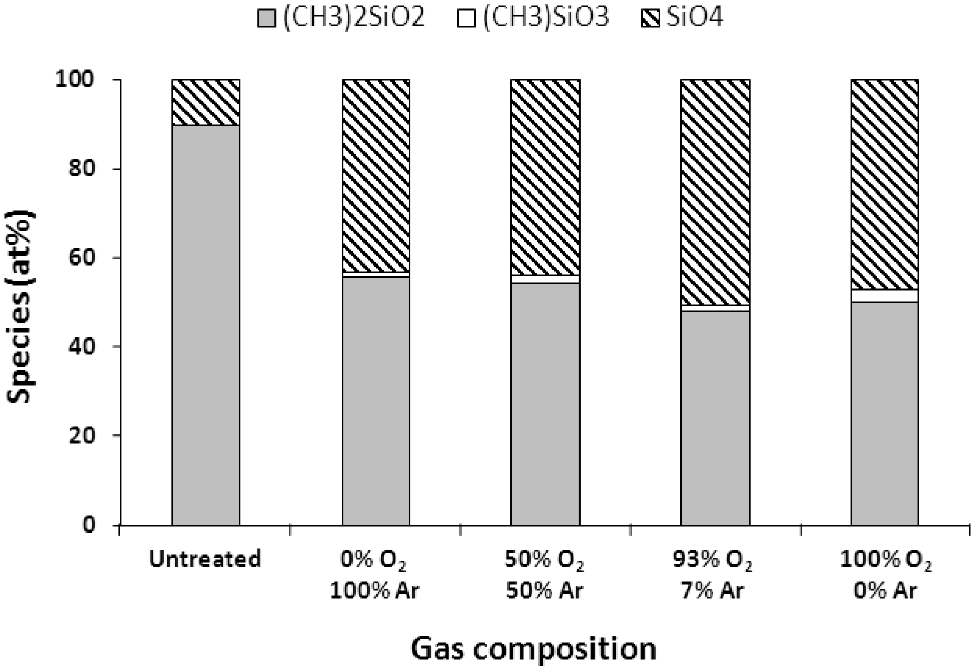


Figure 14. Percentages of silicon species 14 days after treatment on untreated and oxygen, argon and different oxygen and argon mixtures LPP treated PDMS surface with 25W for 120s. Curve fitting of Si2p$_{3/2}$ photopeaks. XPS experiments.

Finally, for evaluating adhesion, T-peel tests were carried out in untreated and 93vol% O_2+7vol% Ar LPP treated PDMS/acrylic adhesive tape joints. Adhesive joints were made with 93vol% O_2+7vol% Ar LPP treated PDMS immediately and after being stored in open air for 3 and 14 days after treatment. Figure 15 shows that adhesion of PDMS increases noticeably (from 22 to 226 N/m) by treatment with LPP plasma under optimal conditions, and furthermore the adhesion is maintained for 14 days after treatment.

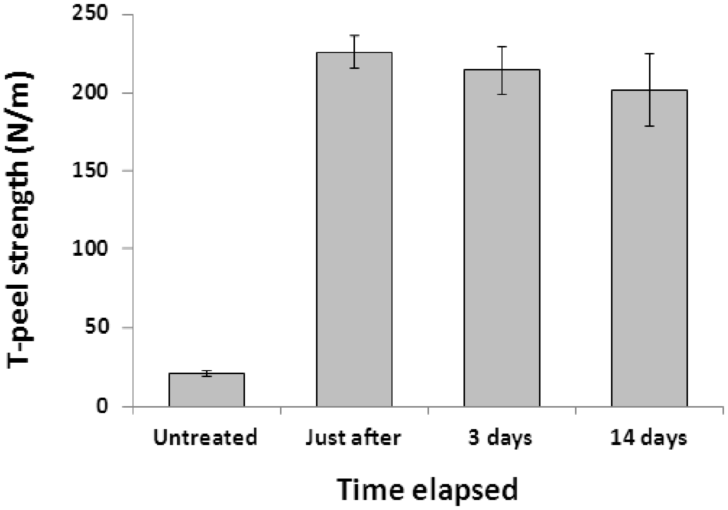


Figure 15. T-peel strength values of untreated and 93vol% O_2+7vol% Ar LPP treated PDMS/acrylic adhesive tape joints made at different times after treatment. LPP treatment conditions : 25W, 300mTorr, 2min.

4. Conclusions

The use of statistical design of experiments has been proved useful in optimizing adhesion and minimizing hydrophobic recovery in oxygen + argon mixtures LPP treated PDMS. The working pressure was the parameter influencing more the surface modification and inhibiting more the hydrophobic recovery of LPP treated PDMS surface. Furthermore, the duration of the plasma treatment, the gas composition and the power influenced the effectiveness of the LPP treatment of PDMS. The optimal conditions for maximizing the surface modifications and adhesion, and minimizing the hydrophobic recovery in LPP treated PDMS were the use of 93vol% O_2 + 7vol% Ar mixture, 300 mTorr of working pressure, 25 W of power and 120 seconds. Adhesion of LPP treated PDMS stored under open air was maintained up to 14 days.

Acknowledgments. This study was carried out in the framework of COST MP1101 project.

References

[1] F. Abbasi, H. Mirzadeh, A. A. Katbab, Modification of polysiloxane polymers for biomedical applications: a review, Polym. Int. 50 (2001) 1279 – 1287.

[2] C. A. Heaton, Polymers, in: J. P. Candlin (Ed.), The Chemical Industry, Springer Publishers, New York (NY, USA), 1986, pp. 3 – 63.

[3] R. F. Patterson, Silicones, in: H. Dodiuk, S. H. Goodman (Eds.), Handbook of Thermoset Plastics, second ed., William Andrew Publishing, Norwich (NY, USA), 1999, pp. 468 – 497.

[4] J. R. Hollahan, G. L. Carlson, Hydroxylation of polydimethylsiloxane surfaces by oxidizing plasmas, J. Appl. Polym. Sci. 14 (1970**)** 2499 – 2508.

[5] M. Morra, E. Occhiello, R. Marola, F. Garbassi, P. Humphrey, D. Johnson, On the aging of oxygen plasma-treated polydimethylsiloxane surfaces, J. Colloid Interf. Sci. 1 (1990**)** 11 – 24.

[6] M. J. Owen, P. J. Smith, Plasma treatment of polydimethylsiloxane, J. Adhes. Sci. Technol. 8 (1994) 1063 – 1075.

[7] D. B. H. Chua, H. T. Ng, S. F. Y. Li, Spontaneous formation of complex and ordered structures on oxygen-plasma-treated elastomeric polydimethylsiloxane, Appl. Phys. Lett. 6 (2000) 721 - 723.

[8] S. Béfahy, P. Lipmik, T. Pardoen, C. Nascimento, B. Patris, P. Bertrand, S. Yunus, Thickness and elastic modulus of plasma treated PDMS silica-like surface layer, Langmuir 5 (2009) 3372 - 3375.

[9] K. Fateh-Alavi, M. E. Núñez, S. Karlsson, U. W. Gedde, The effect of stabilizer concentration on the air-plasma-induced surface oxidation of crosslinked polydimethylsiloxane, Polym. Degrad. Stab. 1 (**2002**) 17 - 25.

[10] B. Olander, A. Wirsen, A. C. Albertsson, Oxygen microwave plasma treatment of silicone elastomer: Kinetic behavior and surface composition, J. Appl. Polym. Sci. 91 (2004) 4098 - 4104.

[11] J. Kim, M. K. Chaudhury, M. J. Owen, Hydrophobicity loss and recovery of silicone HV insulation, IEEE T. Dielect. El. In. 6, (1999) 695 - 702.

[12] J. Bacharouche, P. Kunemann, P. Fioux, M. F. Vallat, J. Lalevée, J. Hemmerlé, V. Roucoules, A simple method for fabrication of filler-free stretchable polydimethylsiloxane surfaces, Appl. Surf. Sci. 270 (2013) 64 - 76.

[13] J. L. Fritz, M. J. Owen, Hydrophobic recovery of plasma-treated polydimethylsiloxane, J. Adhesion 54 (1995) 33 - 45.

[14] E. P. Everaert, H. C. Van der Mei, J. de Vries, H. J. Brusscher, Hydrophobic recovery of repeatedly plasma-treated silicone rubber. Part 1: Storage in air, J. Adhes. Sci. Technol. 9 (1995) 1263 - 1278.

[15] R. A. Lawton, C. R. Price, A. F. Runge, W. J. Doherty III, S. Scott-Saavedra, Air plasma treatment of submicron thick films: Effect of oxidation time and storage conditions, Colloid. Surface. *A* 253 (2005) 213 - 215.

[16] T. Hino, Y. Igarashi, Y. Ymauchi, M. Nishikawa, Surface wettability of silicon rubber after irradiation with a glow discharge plasma, Vacuum 83 (2009) 506 - 509.

[17] S. Bhattacharya, A. Datta, J. M. Berg, S. Gangopadhyay, Studies of surface wettability of poly(dimethyl) siloxane (PDMS) and glass under oxygen-plasma treatment and correlation with bond strength, J. Microelectromech*. S*. 14 (2005) 590 - 597.

[18] J. Y. Lai, Y. Y. Lin, Y. L Denq, S. S. Shyu, J. K. Chen, Surface modification of silicone rubber by gas plasma treatment, J. Adhes. Sci. Technol. 10 (1996) 231 - 242.

[19] J. Kim, M. K. Chaudhury, M. J. Owen, Hydrophobic recovery of polydimethylsiloxane elastomer exposed to partial electrical discharge, J. Colloid Interf. Sci. 226 (2000) 230 - 236.

[20] R. L. Williams, D. J. Wilson, N. P. Rhodes, Stability of plasma-treated silicone rubber and its influence on the interfacial aspects of blood compatibility, Biomaterials 25 (2004) 4659 - 4673.

[21] H. T. Kim, O. C. Jeong, PDMS surface modification using atmospheric pressure plasma, Microelectron. Eng. 88 (2011) 2281 - 2285.

[22] H. Hillborg, M. Sandelin, U. W. Gedde, Hydrophobic recovery of polydimethylsiloxane after exposure to partial discharges as a function of crosslink density, Polymer 42 (2001) 7349 - 7362.

[23] A.R. Sena, G.L. Velasques Jr., I.K. Barretto, S.A. Assis, *Application of Doehlert experimental design in the optimization of experimental variables for the Pseudozyma sp. (CCMB 306) and Pseudozyma sp. (CCMB 300) cell lysis,* Food Sci. Technol (Campinas) 32 (2012) 762 - 767.

[24] E.P. Taffin de Givenchy, S. Amigoni, C. Martin, G. Andrada, L. Caillier, S. Géribaldi, F. Guittard, Fabrication of superhydrophobic PDMS surfaces by combining acidic treatment and perfluorinated monolayers, Langmuir 25 (2009) 6448 - 6453.

[25] J.Y. Lay, Y.L. Denq, J.K. Chen, L.Y. Yuan, Y.Y. Lin, S.S. Shyu, Peel strength improvement of silicone rubber film by plasma pretreatment followed by graft copolymerization, J. Adhesion Sci. Technol. 9 (1995) 813 - 822.

[26] B. Olander, A. Wirsén, A.C. Albertsson, Silicone elastomer with controlled surface composition using argon or hydrogen plasma treatment, J. Appl. Polym. Sci. 90 (2003) 1378 - 1383.

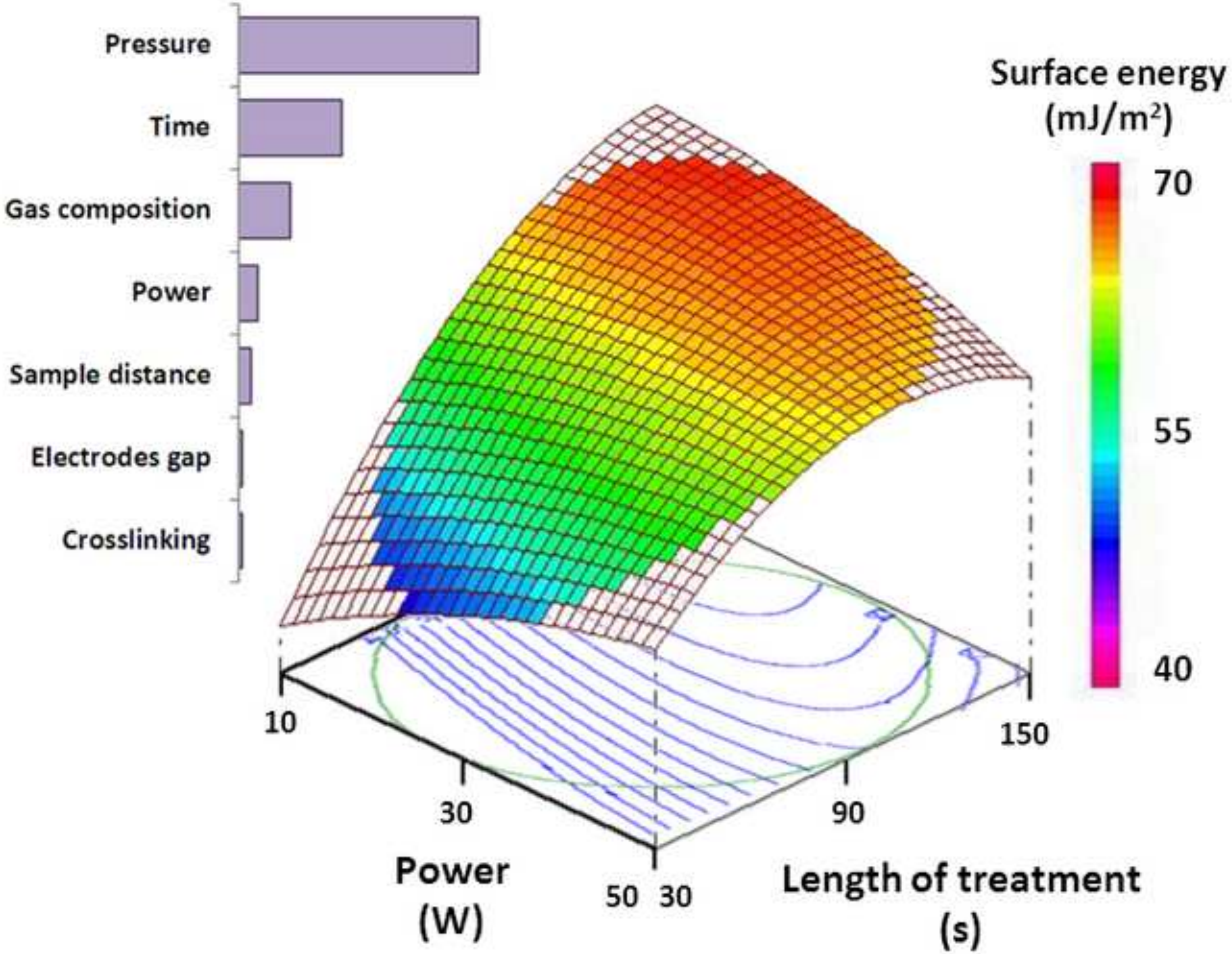
[27] N. De Geyter, R. Morent, T. Jacobs, F. Axisa, L. Gengembre, C. Leys, J. Vanfleteren, E. Payen, Remote atmospheric pressure DC glow discharge treatment for adhesion improvement of PDMS, Plasma Process. Polym. 6 (2009) S406 – S411.

[28] B.K. Kim, K.S. Kim, C.E. Park, C.M. Ryu, Improvement of wettability and reduction of aging effect by plasma treatment of low-density polyethylene with argon and oxygen mixtures, J. Adhesion Sci. Technol. 16 (2002) 509 – 521.

[29] A. Schültze, J.Y. Jeong, S.E. Babayan, J. Park, G.S. Selwyn, R.F. Hicks, The atmospheric pressure plasma jet: A review and comparison to other plasma sources, IEEE T. on Plasma Sci. 26 (1998) 1685-1694.

[30] C. de Menezes-Atayde, L. Doi, Highly stable hydrophilic surfaces of PDMS thin layer obtained by UV radiation and oxygen plasma treatments *Phys. Status Solidi C* 7 (2010) 189 - 192.

Graphical Abstract (for review)



FIGURES

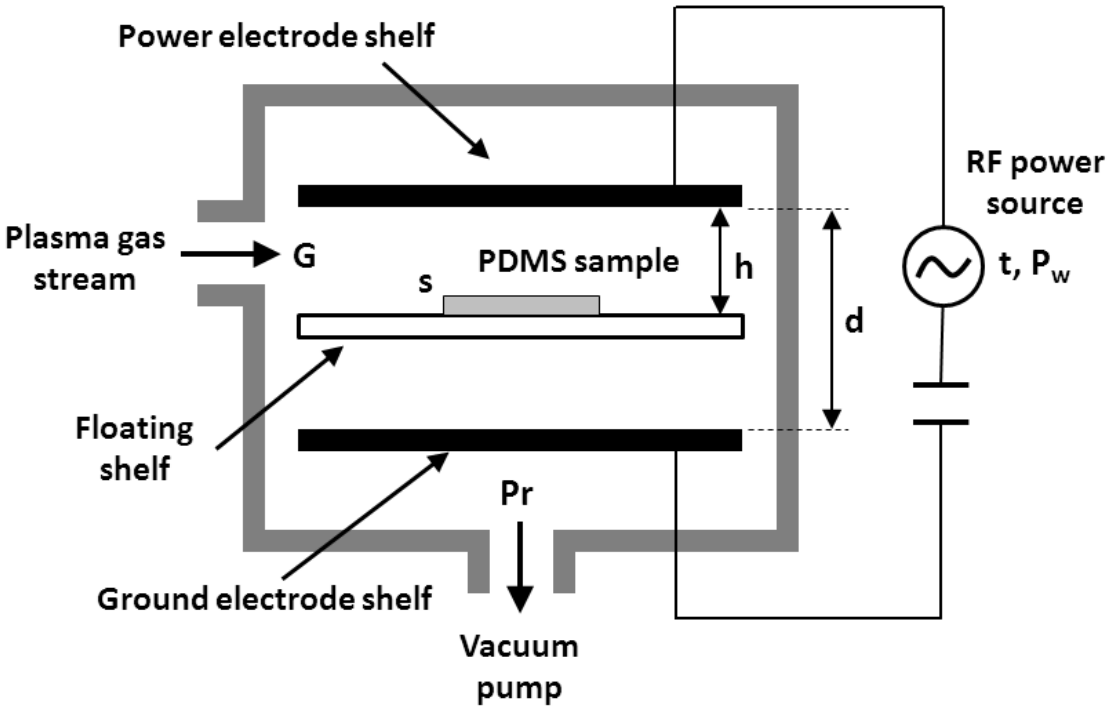


Figure 1

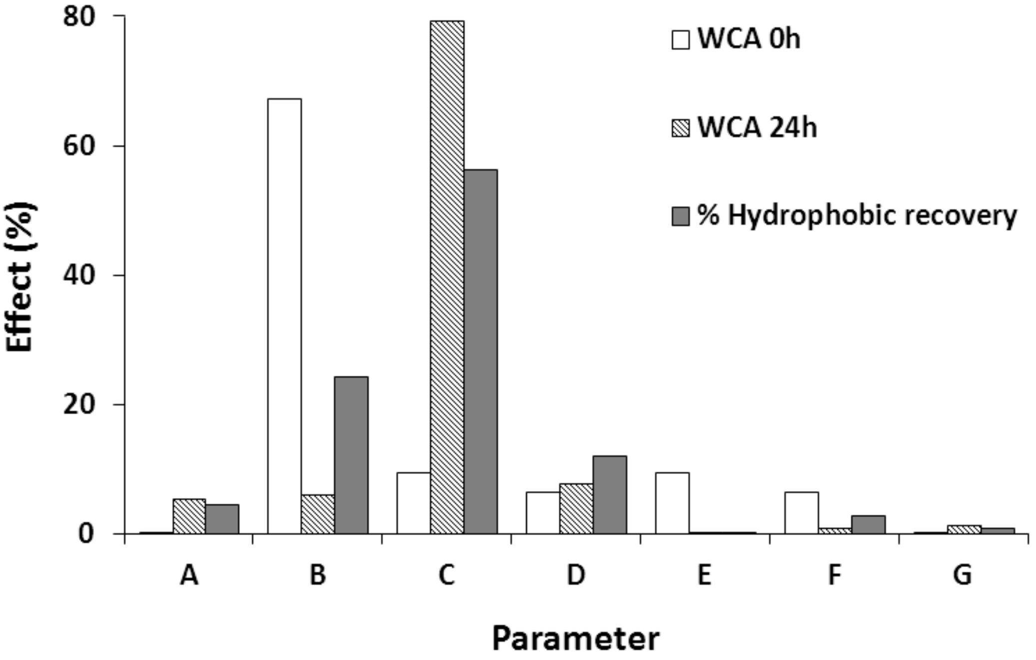

80
60
40
20
0
Effect (%)
A
B
C
D
E
F
G
Parameter
□ WCA 0h
▨ WCA 24h
■ % Hydrophobic recovery

Figure 2

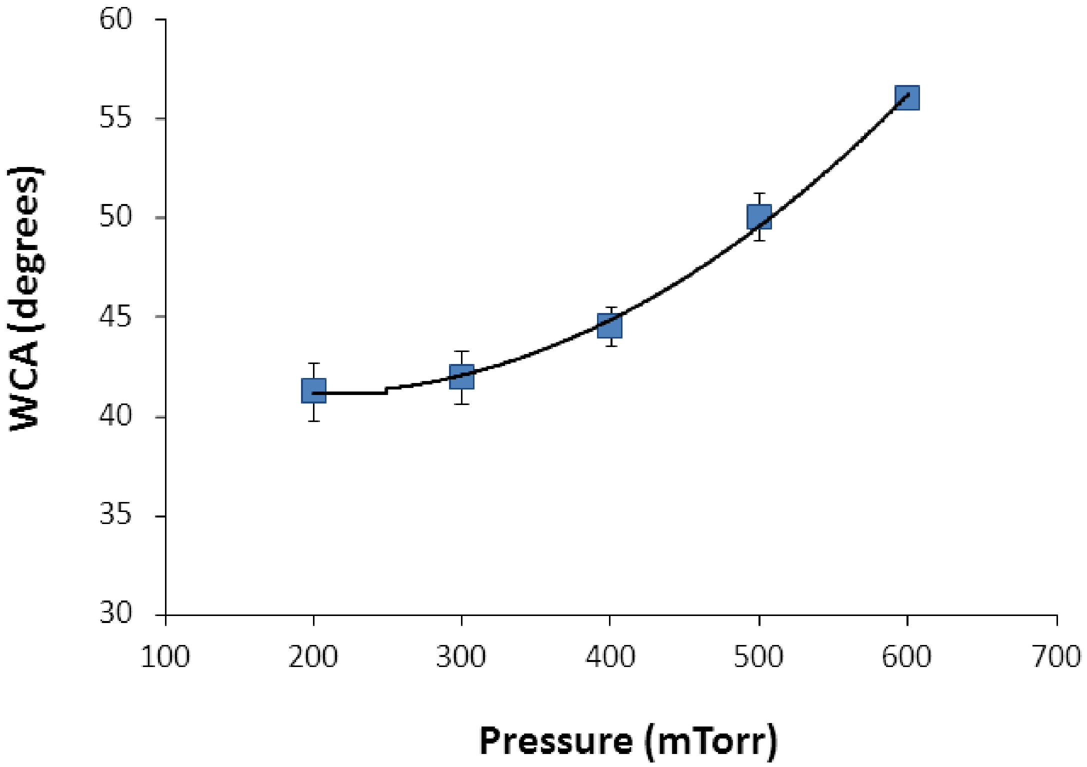

60
55
50
45
40
35
30
WCA (degrees)
100
200
300
400
500
600
700
Pressure (mTorr)

Figure 3

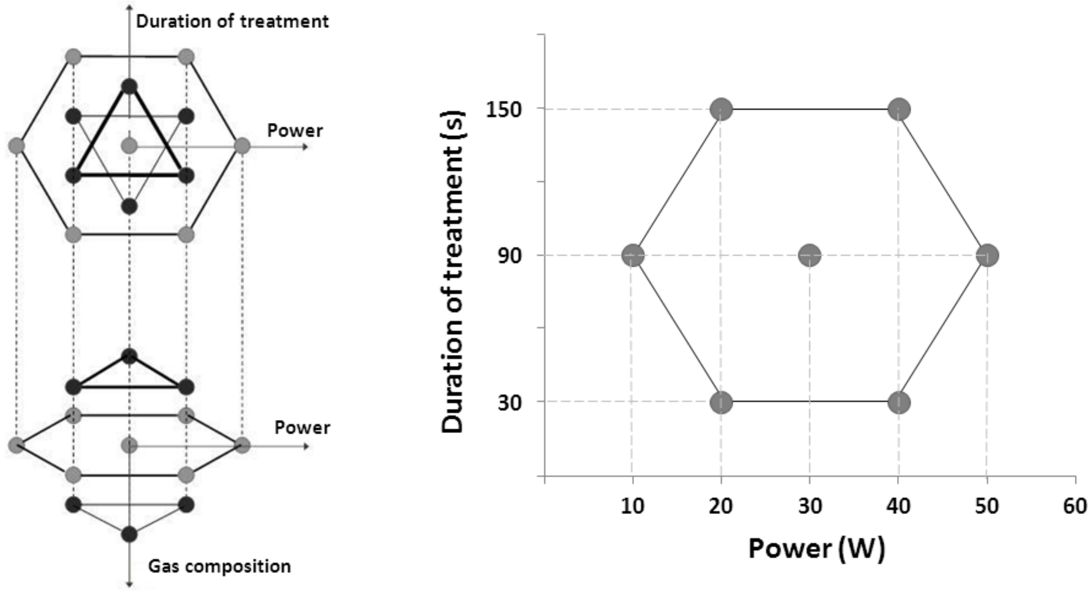

Duration of treatment
Power
Power
Gas composition
Duration of treatment (s)
150
90
30
10
20
30
40
50
60
Power (W)

Figure 4

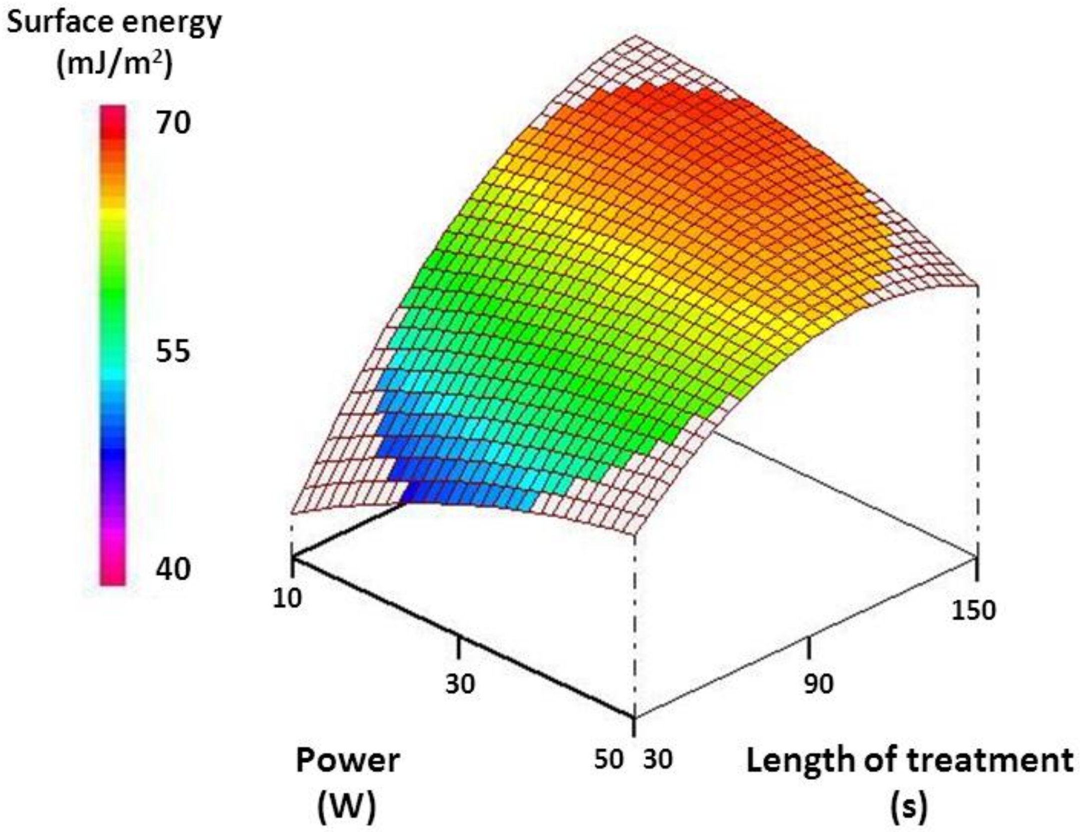

Surface energy
(mJ/m²)
70
55
40
10
30
50
30
90
150
Power
(W)
Length of treatment
(s)

Figure 5a

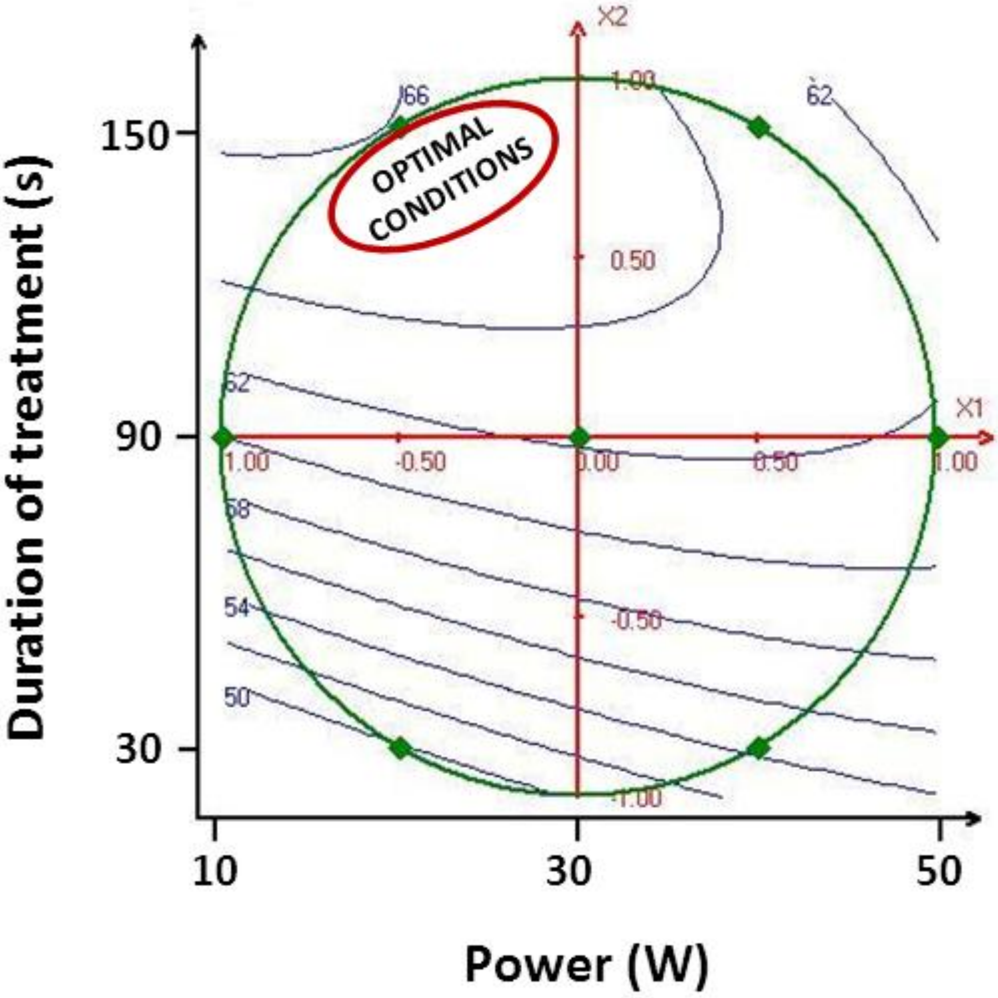

X2
1.00
66
62
150
OPTIMAL CONDITIONS
0.50
Duration of treatment (s)
62
X1
90
1.00
-0.50
0.00
0.50
1.00
58
54
-0.50
50
30
-1.00
10
30
50
Power (W)

Figure 5b

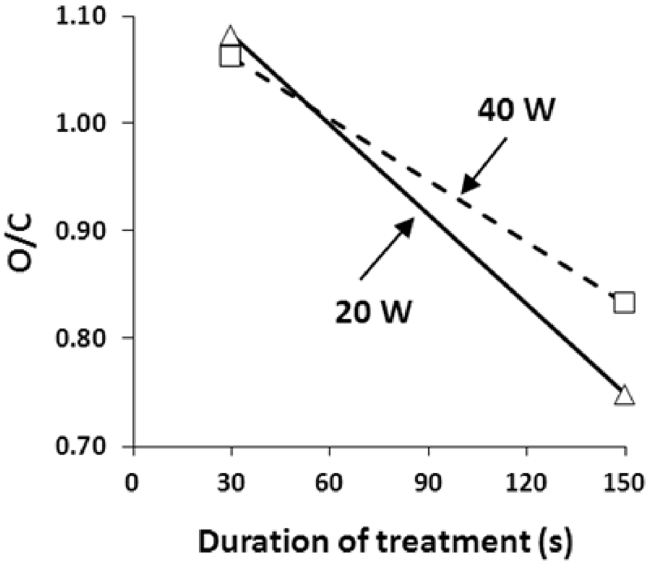

1.10
1.00
0.90
0.80
0.70
O/C
40 W
20 W
0
30
60
90
120
150
Duration of treatment (s)

Figure 6

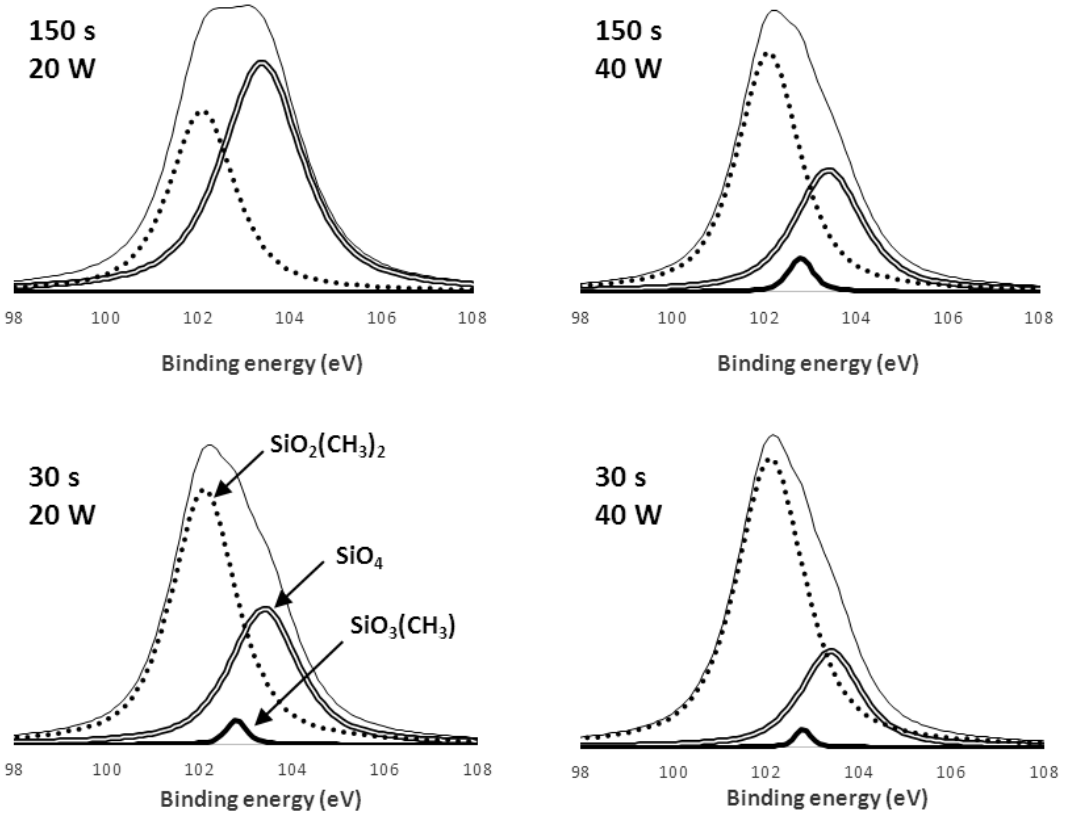

150 s
20 W
98
100
102
104
106
108
Binding energy (eV)
150 s
40 W
98
100
102
104
106
108
Binding energy (eV)
30 s
20 W
$SiO_2(CH_3)_2$
SiO_4
$SiO_3(CH_3)$
98
100
102
104
106
108
Binding energy (eV)
30 s
40 W
98
100
102
104
106
108
Binding energy (eV)

Figure 7

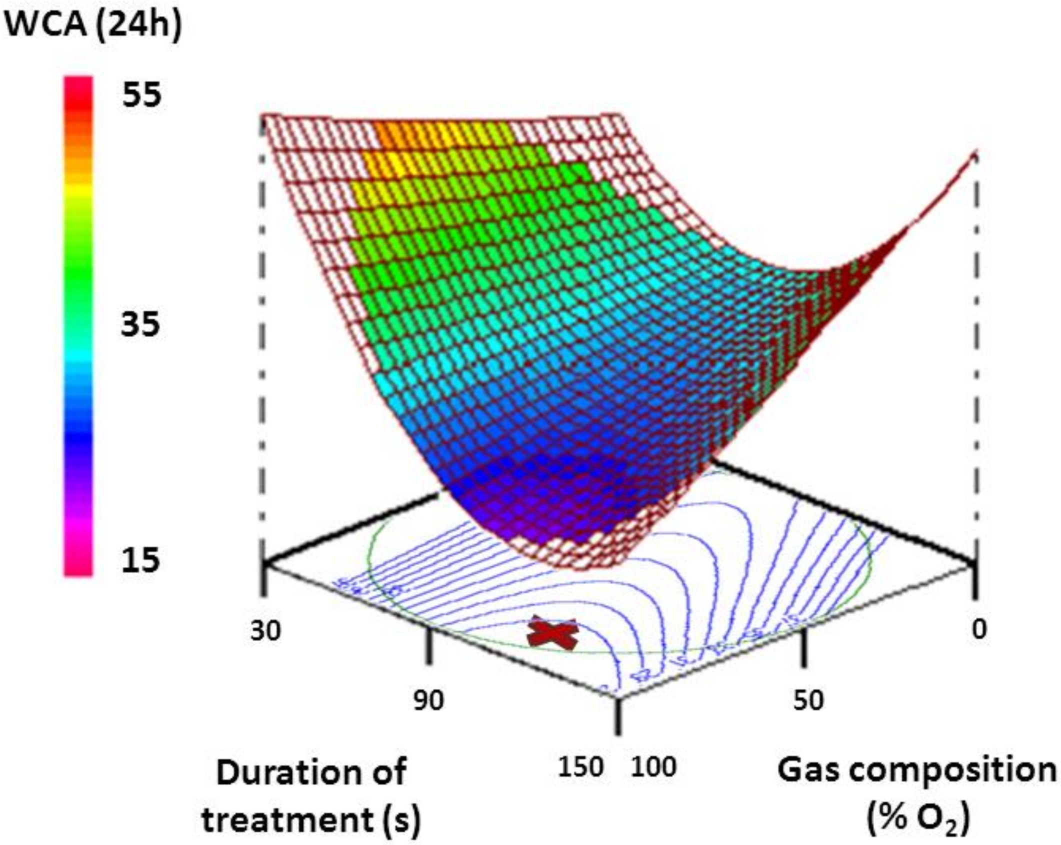

WCA (24h)
55
35
15
30
90
150
100
50
0
Duration of treatment (s)
Gas composition (% O2)

Figure 8

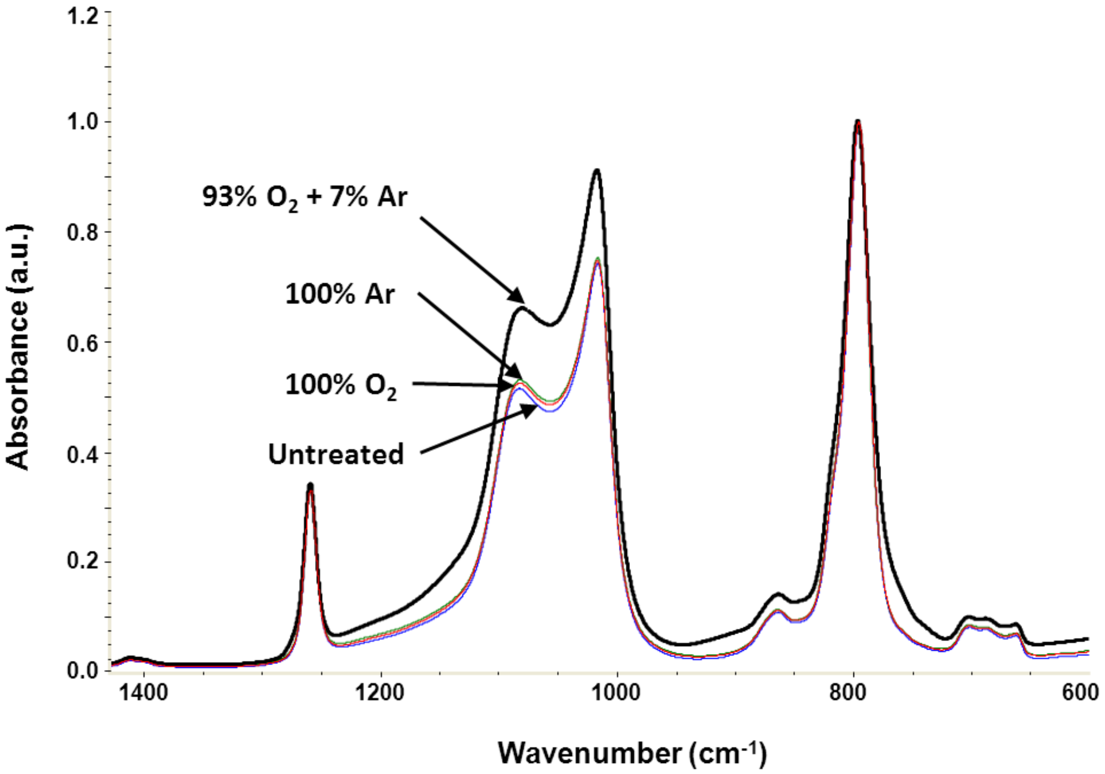

1.2
1.0
0.8
0.6
0.4
0.2
0.0
Absorbance (a.u.)
93% O_2 + 7% Ar
100% Ar
100% O_2
Untreated
1400
1200
1000
800
600
Wavenumber (cm^{-1})

Figure 9a

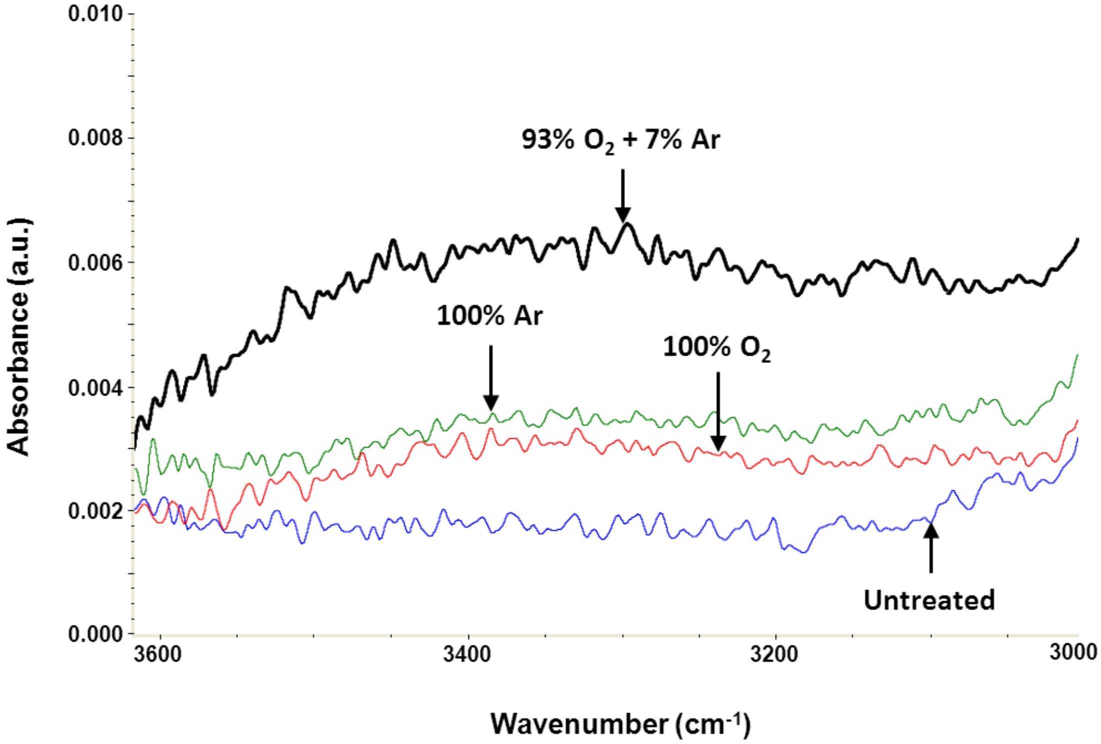

0.010
0.008
0.006
0.004
0.002
0.000
Absorbance (a.u.)
93% O_2 + 7% Ar
100% Ar
100% O_2
Untreated
3600
3400
3200
3000
Wavenumber (cm^{-1})

Figure 9b

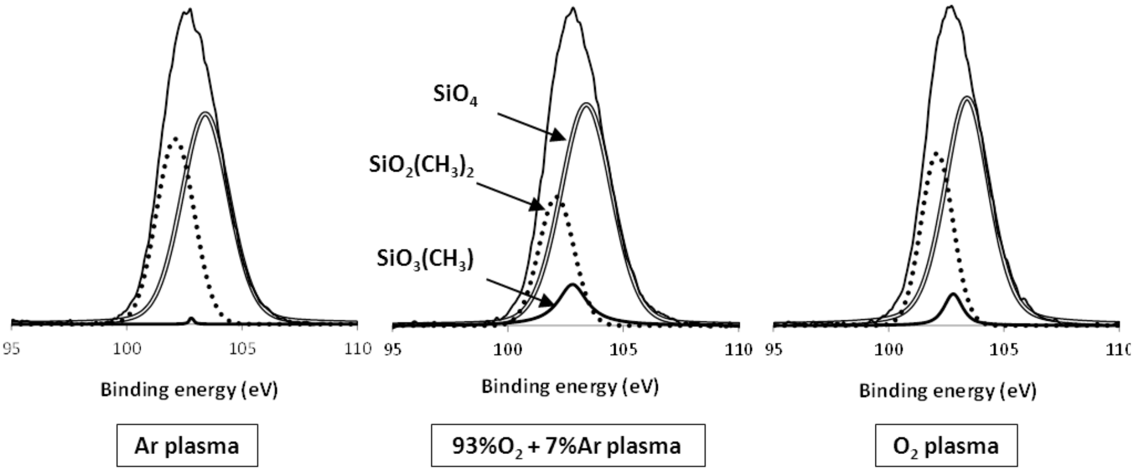

SiO$_4$
SiO$_2$(CH$_3$)$_2$
SiO$_3$(CH$_3$)
95
100
105
110
Binding energy (eV)
Ar plasma
93%O$_2$ + 7%Ar plasma
O$_2$ plasma

Figure 10

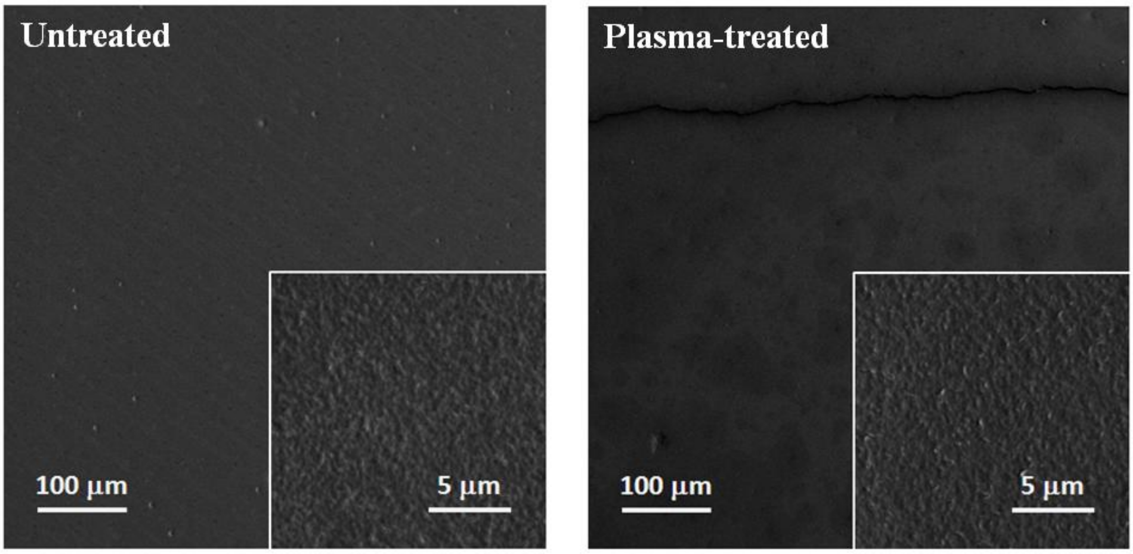


Figure 11

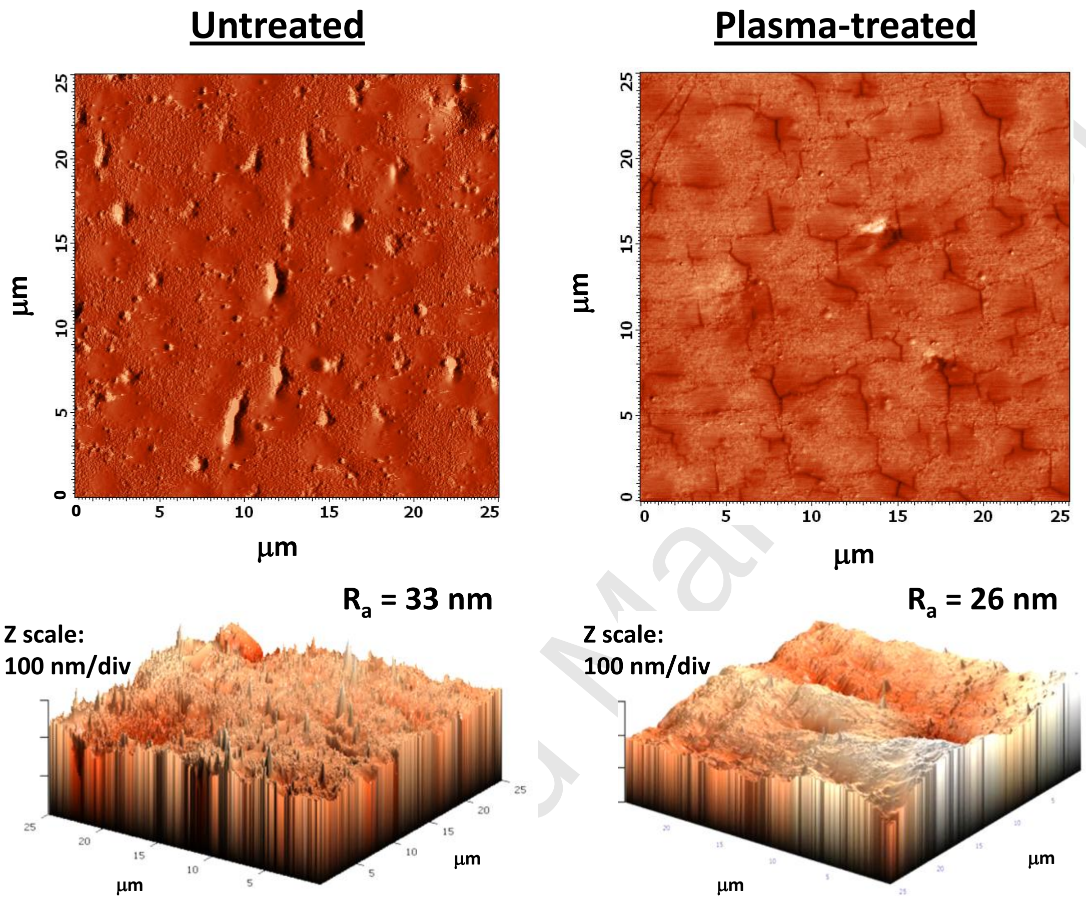

Untreated
Plasma-treated
µm
0
5
10
15
20
25
µm
R$_a$ = 33 nm
R$_a$ = 26 nm
Z scale:
100 nm/div
Z scale:
100 nm/div

Figure 12

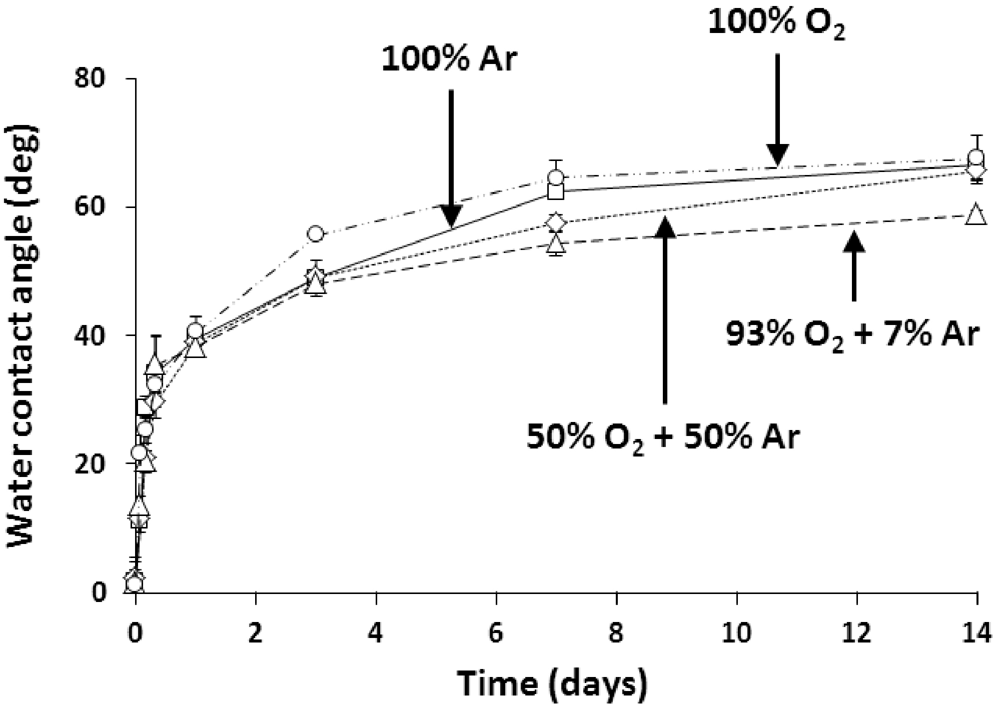

100% O₂
100% Ar
93% O₂ + 7% Ar
50% O₂ + 50% Ar
Water contact angle (deg)
0
20
40
60
80
Time (days)
0
2
4
6
8
10
12
14

Figure 13

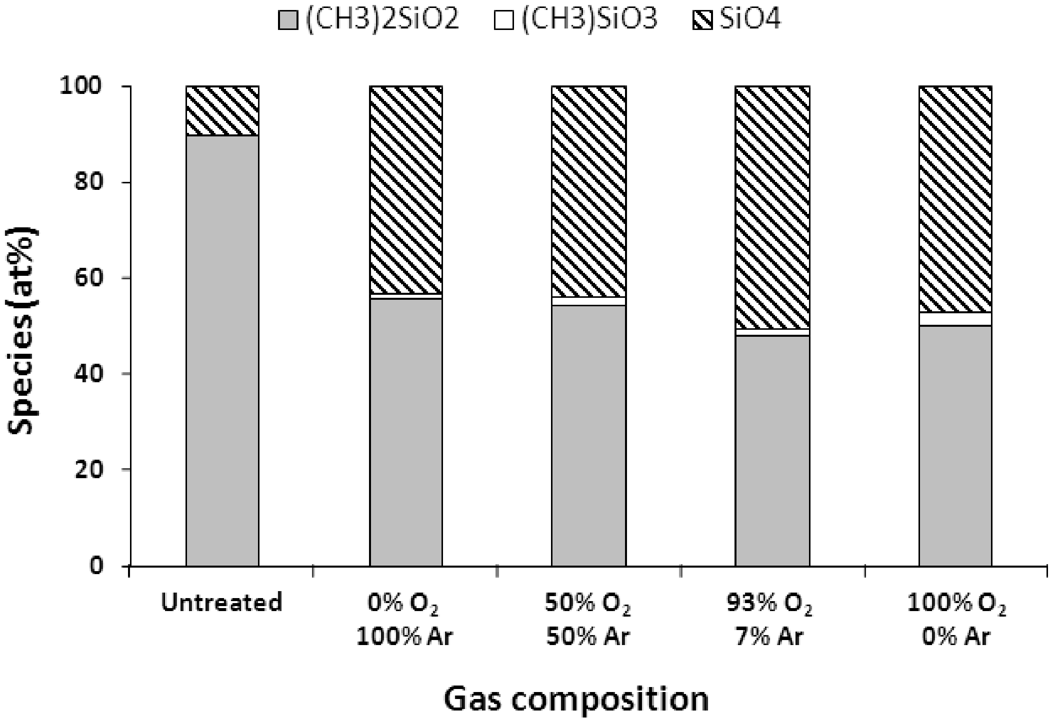

(CH3)2SiO2
(CH3)SiO3
SiO4
100
80
60
40
20
0
Species (at%)
Untreated
0% O_2 100% Ar
50% O_2 50% Ar
93% O_2 7% Ar
100% O_2 0% Ar
Gas composition

Figure 14

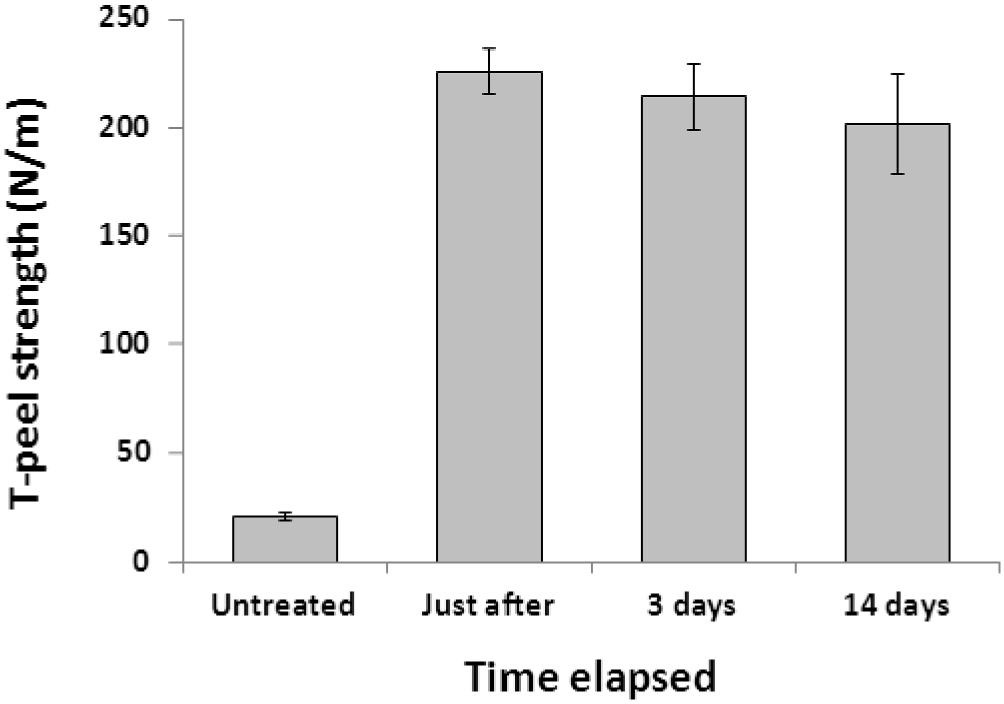

250
200
150
100
50
0
T-peel strength (N/m)
Untreated
Just after
3 days
14 days
Time elapsed

Figure 15