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Vapor phase surface functionalization under ultra violet activation of parylene thin films grown by chemical vapor deposition

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ABSTRACT

Various reactive gas phase treatments have been investigated as surface functionalization dry processes with the goal to improve the wettability of parylene C films, keeping good optical properties in the visible range. The films were grown on different substrates by chemical vapor deposition with thicknesses ranging from 300 to 1630 nm. The polymer surface was treated under ultra violet (UV) irradiation at 254 nm in reactive atmospheres including He, H₂O, H₂O₂, O₂ and ambient air. The UV/O₂ treatment is the most efficient since the water contact angle decreases from 100° to 6° while the transmittance is maintained at 90% in the visible wavelengths. Furthermore it exhibits long life stability. The functionalization mechanism is discussed in relation with previous reports.

Keywords:

Parylene films
UV irradiation
Aging
Surface functionalization
Optical coatings
Surface composition

1. Introduction

The not substituted poly(*para*-xylylene), known as parylene N or PPXN, shows excellent optical, electrical and thermal properties. In addition, its chemical stability and biocompatibility allows its use in bio-medical applications. Parylene coatings can be synthesized by the Gorham method, a chemical vapor deposition (CVD) process that produces conformal, pin-hole free and high purity thin films without any use of solvent [1]. Nevertheless, one of the principal limitations of this polymer is its hydrophobic property which can lead to adhesion problems when it is combined with other materials in advanced devices [2,3].

Indeed, polymers exhibit frequently low surface energies (<30–40 mJ/m²) and consequently a low hydrophilicity. For instance, we have measured the surface energy of the poly(2-chloro-*para*-xylylene) (namely, parylene C or PPXC) by the Owens–Wendt method and we found approximately 40 mJ/m². Such surfaces are chemically inert and are not readily wet by other materials resulting in a poor adhesion. A solution to this problem is to chemically or physically modify the polymer surface. For this goal, various surface modification processes have been proposed, including mechanical (surface roughening), chemical (reduction, oxidation and grafting), and physical (plasma and ion or electron bombardment) treatments [4,5]. These various processes can be classified into two groups: the wet and the dry routes.

Previous works have been reported on the surface functionalization of parylene. The wet route was explored for parylene N or C surfaces with or without ultra violet (UV) activation. For instance, the UV/acrylamide [6] and UV/2-methacryloyloxyethyl phosphorylcholine–benzophenone treatments [7] permitted to divide by about 2 the water contact angle of the modified surfaces. The state of the art on the wet treatments without UV activation gave, under the best conditions, a final contact angle of 10° compared to initial contact angles of 75–95° [8,9].

The dry treatments using for instance reactive vapor phases without plasma activation are particularly interesting for parylene thin films because they can be applied directly in a CVD reactor or in sequence with the CVD process in a related reactor. This is a clean multi-step process particularly convenient to control the surface properties of the parylene films. Two examples are H₂O vapor activation by a hot W filament for the surface treatment of parylene AF-4 (fluorinated parylene derivative) [10] and UV/air treatment of parylene C and N [5,11–13]. However the functionalization efficiency of these dry processes was generally lower than using the wet chemistry since the water contact angle decreased from 90° to only 56–58° [5].

From these results and other literature data on different polymers [4,14–17], we observe that only a few studies deal with the use of dry processes and, furthermore, they revealed a limited efficiency for the surface modification of the polymer. Previous works were reported on the functionalization of parylene thin films by gas phase photo-activation [5,11,12]. The Table 1 summarizes the most relevant results. All these studies have used air as reactive atmosphere and the influence of the experimental parameters was explored in a relatively narrow range. The aims of these works were (i) to change the wettability and subsequently adhesion on other materials [5], (ii) to improve the

Table 1

Comparison of relevant literature studies on the surface functionalization of parylene thin films.

Parameter	Ref. [5]	Ref. [11]	Ref. [12]	This work
Kind of parylene	N and C	N and C	N	C
Film thickness (nm)	3000	200–3000	330	300–1630
UV irradiation wavelength (nm)	254	<300	254	254
Dose (mj/cm ²)	500–10 000	No data	12 000–43 000	5600–67 000
Irradiation time (min)	13–255	No data	420–1440	10–120
Reactive gas	Air	Air	Air	H ₂ O, H ₂ O ₂ , O ₂ , air, and He
Substrate	Si	Quartz and glass	Si	Si and glass

solubility of parylene films for photo-masking systems [11] and (iii) to gain a better insight into the UV radiation impact on the thermal and electrical properties of parylene in order to use it in UV environment [5,12]. None of these works on parylene films aimed to improve both the hydrophilicity keeping constant the optical properties in the visible range or to study the aging of these modified surfaces.

To complete the above studies, we have investigated the photo-activation of different reactive gas phases for the functionalization of the surface of parylene thin films. Our goal was to develop an efficient surface treatment that can be applied in a CVD reactor in order to control the hydrophilicity of the films without changing their bulk properties, especially the transparency in the visible range. The chlorinated derivative poly(2-chloro-*para*-xylylene), PPXC, was used as parylene thin film. In addition to the surface treatment conditions, the influence of the film thickness and the aging of the modified surfaces are reported.

2. Experimental details

2.1. UV irradiation reactor

The experimental set up was previously used for photo-CVD of copper layers [18]. The parylene thin films were placed in a vertical stainless steel reactor (14.5 cm in diameter). The samples were maintained at room temperature under the atmospheric pressure of a controlled ambience. The reactive vapor was transported at room temperature with an inert carrier gas (He) from a thermostated bubbler (20 °C) to the reactor through gas lines. All gas flow rates were monitored using mass flowmeters. The mole fractions of reactive vapors (H₂O and H₂O₂) were determined by adjusting the flow rate of the carrier gas (He) and the vapor pressure of the liquid compound in the bubbler according to the method described elsewhere [19]. The gas streams entered the reactor through a ring of copper tube (ring diameter 10 cm) perforated of several holes. So, the vapor was uniformly injected normal to the surface of the PPXC films.

UV illumination was produced using a low-pressure Hg lamp (Vilber Lourmat) through an optical grade silica window (Suprasil), 10 cm in diameter, and the gas distribution ring. The radiation was unfocused and directed perpendicular to the surface of the films. The main emission at 254 nm represented more than 80% of the radiative power while the radiation at 185 nm was partially absorbed by the air stream used for the air-cooling of the lamp. The distance between the lamp and the samples was about 5 cm. These conditions produce a radiation power of approximately 9.3 mW/cm² on the films. A period of about 20 min was required to reach the stationary value of the radiation power.

2.2. Starting materials and methods

The PPXC thin films were deposited on glass and silicon substrates by the CVD process known as the Gorham method [1]. Various film thicknesses have been deposited in the range 300–1630 nm. The

thickness uniformity was better than 5% on substrates of 7 cm in diameter. For further vapor phase treatments, the samples were cut in the same substrate in order to get similar film thickness. The different gases or vapors were O₂, H₂O, H₂O₂ and He, this last one being also used as dilution gas. The mole fractions were controlled for the various treatments.

The UV/He surface treatments of the PPXC films were achieved to study the effects of UV radiation on the polymer surface without any reactive gas. The UV functionalization treatment under oxygen stream (namely UV/O₂) was investigated for various O₂ mole fractions. For these treatments, the total gas flow rate was also controlled in order to take into account the residence time of the reactive molecules in the reactor.

For the UV/H₂O or UV/H₂O₂ treatments, the water and hydrogen peroxide vapors were transported by a low He flow rate and their mole fractions were fixed. The Clapeyron equation gives the vapor pressure of a compound i (P_i) as a function of the temperature. The vapor pressure of water (P_{water}) and pure hydrogen peroxide ($P_{\text{H}_2\text{O}_2}$) at 20 °C are respectively: $P_{\text{water}} = 2.32$ kPa and $P_{\text{H}_2\text{O}_2} = 0.20$ kPa [20]. The hydrogen peroxide was an aqueous solution of 35 wt.% of H₂O₂ in water. This information permits to calculate the real vapor pressure of the H₂O₂ solution ($P_{\text{H}_2\text{O}_2\text{-sol}}$) using the Raoult law:

$$P_{\text{H}_2\text{O}_2\text{-sol}} = X_{\text{water}}P_{\text{water}} + X_{\text{H}_2\text{O}_2}P_{\text{H}_2\text{O}_2} \quad (1)$$

where X_{water} and $X_{\text{H}_2\text{O}_2}$ are the mole fractions of H₂O and H₂O₂ in the liquid solution. The calculation gives: $P_{\text{H}_2\text{O}_2\text{-sol}} = 2.53$ kPa at 20 °C. In a first approximation, the mole fraction in the input gas phase of a reactant i ($X_{i\text{-gas}}$) at 20 °C is expressed by the relation:

$$X_{i\text{-gas}} = P_i / P \quad (2)$$

where P is the total pressure. As a result, under atmospheric pressure and at 20 °C, the mole fraction of H₂O and H₂O₂ in the gas phase at the entrance of the reactor is: $X_{\text{water-gas}} = 2.3\%$ and $X_{\text{H}_2\text{O}_2\text{-gas}} = 1.8\%$. The experimental conditions are summarized in the Table 2.

2.3. Characterization techniques

The samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a VG Escalab MKII spectrophotometer, which operated with a nonmonochromatized Mg K α source (1253.6 eV) at 150 W in order to limit the radiation damage of the surface during analysis.

Contact angles of water droplets were measured at room temperature with a Digidrop instrument in ambient air. The water droplet volume was typically 2 μ l. The average value of at least three measurements at different points on the sample surface was determined. The stability of the room temperature (22 ± 2 °C) and relative humidity ($34 \pm 5\%$) were checked for each measurement. Analyses were performed a few minutes after the surface treatment to limit the air exposure of the samples. For some of them, they were submitted to this ambience for long periods (a few hours to several days) to study the aging effect.

The UV-Vis-NIR spectrophotometry was used to determine the transmittance of the PPXC films deposited on glass substrates in the wavelength range 250–900 nm (Perkin Elmer Lambda 19 spectrophotometer). Fourier transform infra red (FTIR) spectroscopy either in transmission or Attenuated Total Reflection (ATR) modes were performed on PPXC films grown on glass or silicon substrates between 400 and 4000 cm⁻¹ using a NICOLET 5700 FTIR apparatus.

3. Results and discussion

3.1. Wettability

The results on the wettability (water contact angle) will be discussed first because this is the main surface property of parylene films that we want to control. Different reactive gases have been used

Table 2

Experimental conditions of vapor phase surface treatments applied for the functionalization of parylene C thin films (total pressure 101.3 kPa; sample temperature 25 °C).

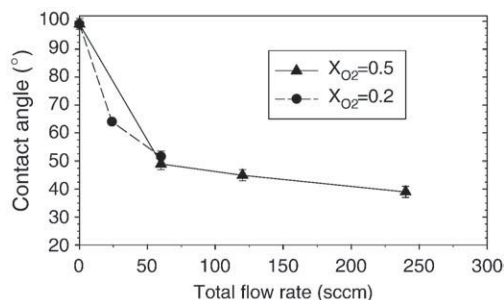
Reactive gas species	Total flow rate Q_T (sccm)	Reactive gas flow rate Q_i (sccm)	Sample temperature T (°C)	Total pressure P (kPa)	Mole fraction X_i (%)	Treatment time τ (min)	UV activation (254 nm)
He	44	44	25	101.3	1	10–120	On
H ₂ O ^a	17	0.4	25	101.3	2.3	10–30	On/off
H ₂ O ₂ ^a	17	0.3	25	101.3	1.8	10–30	On/off
Air	–	–	25	101.3	2	10–45	On
O ₂ /He ^b	24–240	12–120	25	101.3	0.2–1	10–120	On

^a Vapor transported using He as carrier gas.^b Controlled O₂ partial pressure.

in this study and, for each experiment, the treatment time τ was the principal parameter. However, for the UV/O₂ treatment, the influence of the total flow rate Q_T and the oxygen mole fraction X_{O_2} were also investigated. For instance, the Fig. 1 shows that the contact angle of the parylene surface decreases with the increase of the total flow rate (all other parameters were kept constant). Above 60 sccm (cubic centimeters per minute under standard conditions) the total flow rate Q_T has no significant influence. This Q_T value is likely a frontier between a transient state and a stationary state. The minimal total flow rate needed to improve the hydrophilicity is around 60 sccm. Similarly the contact angle decreases when the oxygen mole fraction increases, then it stabilizes for mole fractions higher than 0.2 (Fig. 2). A stationary state is found for X_{O_2} in the range 0.2–1.0. These optimal parameters lead to the best efficiency of the treatment with a minimal amount of reactive species. So, these results indicate that it is not necessary to work with high total flow rates and pure oxygen atmosphere. Consequently we have selected 60 sccm as total flow rate and 0.5 as O₂ mole fraction for the future experiments.

We have to emphasize that the efficiency of the gas phase treatment depends on the partial pressure of the reactive gas near the surface of the samples. Depending on the total flow rate, and so on the gas velocity, this partial pressure near the surface can be significantly different from the input of the reactor. Typically, in this geometry, for low total flow rates, the gas stream flows toward the outlet of the reactor which is perpendicular to the ring distribution generating a depletion of the gas species toward the surface of the sample. High gas velocities, *i.e.* Q_T higher than a critical value is required for a uniform gas distribution under atmospheric pressure and then a good control of the partial pressure near the treated surface. This was estimated at 60 sccm. If the efficiency of the treatment was essentially due to phenomena in the gas phase, *e.g.* photolysis of the reactives, thus low residence times of the reactive species (low Q_T) should improve the efficiency. This contrasts with the experimental results, which permits to conclude that the UV treatment essentially acts in the heterogeneous phase since activation is only efficient when the reactive gas sweeps over the surface of the sample.

The wettability (with water droplets) determined for all the treatments are shown in the Fig. 3. It is clear that the treatments which have the greatest impact on the wettability are those using oxygen and air stream under UV irradiation. For instance, the contact

**Fig. 1.** Wettability (water droplets) of UV/O₂ treated PPXC films versus the total gas flow rate Q_T (O₂ + He) for a surface treatment time τ of 30 min and two O₂ mole fractions.

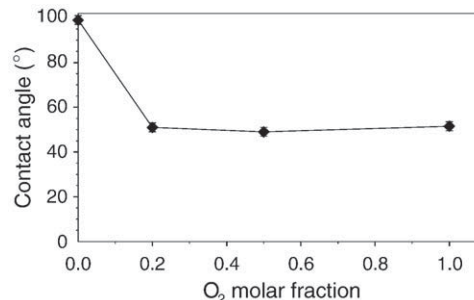
angle is reduced from 100° to about 6° for a UV/O₂ treatment for 120 min. A repeatability study has been realized for the UV/O₂ treatment. Three treatments have been applied to PPXC surfaces in the same conditions ($Q_T = 60$ sccm, $\tau = 120$ min and $X_{O_2} = 0.5$) and the same contact angle was obtained: *c.a.* $6 \pm 1^\circ$. We can compare our results with a relevant study on the surface functionalization of PPXC thin films by UV/air treatment [5]. These authors reported a final contact angle of about $58 \pm 1^\circ$ after irradiation with a dose of 10 000 mJ/cm². In our study, we find comparable values: $62 \pm 3^\circ$ after UV irradiation treatment of 16 700 mJ/cm² under UV/air and $49 \pm 2^\circ$ under UV/O₂.

Some treatments have no influence on the wettability: water vapor and hydrogen peroxide vapor without UV irradiation revealing the great importance of the UV photons. From the data reported in the Figs. 1 and 3 we found typically that the final contact angle after UV/H₂O, UV/H₂O₂ and UV/O₂ treatments is 80°, 75° and 65°, respectively (all the treatment conditions were fixed: $Q_T = 17$ –24 sccm; $\tau = 30$ min). This indicates a better efficiency of the UV/O₂ treatment.

3.2. Optical properties

Our goal for these surface treatments was dual: (i) to decrease the films surface wettability and (ii) to keep the optical transparency the films. The optical transmittance in the UV-Vis range of the films deposited on glass substrates was controlled before and after the treatments. Typically, the films exhibit a high transmittance in the visible wavelengths (*c.a.* 90%) and no significant variation was observed after treatments (film thickness 300 nm). Some treatments trigger off a degradation of the transmittance in the UV range (around 340 nm), *e.g.* UV/He, UV/H₂O₂, UV/H₂O, UV/O₂ and UV/air. By contrast, without UV activation no change in transmittance either in the visible or UV range was observed using these gaseous reactants (Fig. 4).

Comparing the UV/O₂ and UV/He treatments gives an idea of the influence of a reactive and an inert gas phase, respectively. The most damaged samples after 120 min under UV irradiation were those treated under He atmosphere. This reveals a deleterious effect of UV on the parylene thin films (photolytic scission). Interestingly, the samples treated under UV/O₂, which exhibit the best hydrophilicity, undergo a lower loss of transmittance in the UV range than those treated under He: 35% and 55%, respectively. So, during these functionalization

**Fig. 2.** Wettability (water droplets) of UV/O₂ treated PPXC films versus oxygen mole fraction X_{O_2} for a treatment time τ of 30 min (total gas flow rate $Q_T = 60$ sccm).

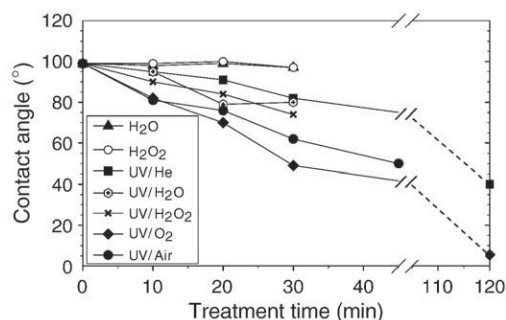


Fig. 3. Influence of the treatment time and the reactive gas atmosphere on the water contact angle of surface treated PPXC films. For the UV/O₂ treatment, the data were obtained for X_{O₂} = 0.5 and Q_T = 60 sccm. For the other treatments the conditions are given in Table 2.

processes at least two mechanisms occur: (i) transformations/reactions in the bulk of the samples induced by UV irradiation and (ii) surface oxidation due to the reactive atmosphere. This second mechanism seems to limit the degradation of the polymer observed under UV solely and maintains good optical properties.

3.3. FTIR analysis

FTIR-ATR and FTIR-Transmission analyses were realized on films before and after surface treatments. The spectra show the C=O stretching vibrations at 1710 cm⁻¹ and a small peak around 1290 cm⁻¹ which can be attributed to C-O. The relative intensity of the C=O peak increases with the treatment time for all the treatments under UV irradiation (Fig. 5). It is particularly clear for the UV/air and UV/O₂ treatments. As a result, the improvement of the wettability observed after those treatments is due to a surface oxidation and then to the formation of C-O and C=O bonds. These results confirm those already found [5,12]. We also noticed a shift of the C=O peak on the FTIR spectra after UV/O₂ treatments depending on the irradiation time. It shifts from 1708 cm⁻¹ to 1710 cm⁻¹

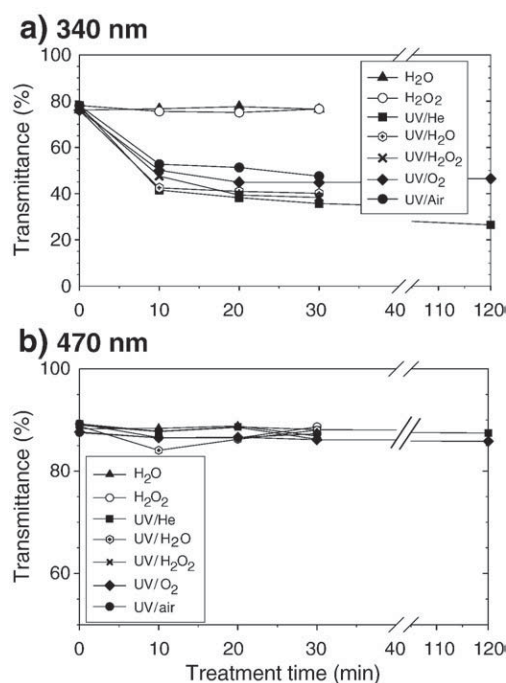


Fig. 4. Influence of the treatment time and the reactive gas atmosphere on the transmittance at two wavelengths of PPXC thin films deposited on glass: (a) at 340 nm and (b) at 470 nm (the film thickness is 300 nm for all samples).

and finally 1718 cm⁻¹ after irradiation during 10, 20 and 120 min, respectively. This shift corresponds to the change from an α,β -unsaturated aldehyde or ketone to an α,β -unsaturated ester or carboxylic acid. This reveals some chemical reactions involved in the functionalization mechanism.

A thorough analysis permits to identify the reactions involving the aliphatic chain and/or the aromatic rings. We observe the C-H stretching vibrations of the methylene (-CH₂-) at 2935 and 2865 cm⁻¹ of the chain. After UV treatments, the intensity of those peaks decreases and the 2865 cm⁻¹ peak is shifted to 2873 cm⁻¹ (after 120 min under UV/O₂). This indicates that the linear aliphatic structure is broken by the UV irradiation and the 2873 cm⁻¹ band is attributed to C-H asymmetric bending vibrations of methyl (-CH₃). Moreover, the band at 1494 cm⁻¹ is assigned to methylene C-H bend vibrations; the intensity of this band decreases after treatment and a new band appears around 1440 cm⁻¹ (C-H asymmetric bend vibrations of methyl). So, it is clear that the oxidation reactions occur in the aliphatic chain. We can also analyze the aromatic ring group frequencies. On the IR spectra a small band is observed around 1612 cm⁻¹; it corresponds to stretching vibrations of aromatic rings (C=C-C) [12]. We find these bands in all spectra, independently of the treatment. This indicates the ring carbons are not involved in the functionalization reactions in the sense that there is no evidence for a ring opening. Moreover, additional bands are observed at 3035 and 3077 cm⁻¹ assigned to the aromatic C-H stretching vibrations and 1051 cm⁻¹ (C-Cl) [21]. The intensity of these three bands decreases slightly by increasing the treatment time. This indicates that the substituents on the aromatic cycles are involved in the functionalization reactions as previously reported [21].

3.4. XPS analysis

XPS analyses of the PPXC films provide information on the chemical structure of the modified parylene surfaces. Analysis of untreated PPXC sample revealed that oxygen was not present on the surface even in the form of an atmospheric contamination layer

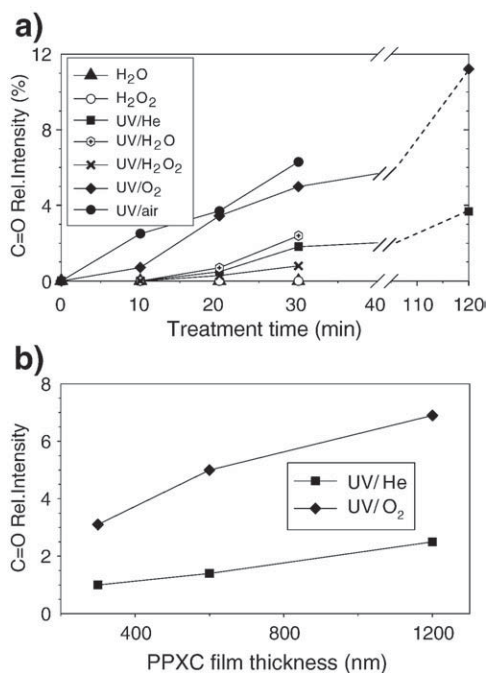


Fig. 5. Variation of the IR relative intensity of the C=O peak (1710 cm⁻¹) as a function of (a) the treatment time (keeping constant the thickness) and (b) the thickness of PPXC films for different reactive gas atmospheres. The data were obtained by ATR spectrometry and were very consistent with transmission measurements. The treatment conditions of (a) and (b) are given in Table 2, excepted for UV/O₂ where Q_T = 60 sccm and X_{O₂} = 0.5. The treatment time in (b) was 2 h.

(Fig. 6). The different elements are assigned to functional groups in Table 3.

The Cl 2p core level shows at least two Cl species corresponding to Cl–C bonds at 200.2 and 201.6 eV. In a previous work, XPS analyses of PPXC thin films also shown two components assigned to Cl 2p_{3/2} and Cl 2p_{1/2} found at 200.8 and 202.4 eV, respectively [8]. The spin orbital splitting was about 1.6 eV. According to this previous report, we assigned our two contributions to Cl 2p_{3/2} and Cl 2p_{1/2} and the splitting is near 1.4 eV for the untreated PPXC films. The difference of the Cl 2p binding energies can be explained by variation in the Cl content of the PPXC layers. Indeed, for various polymers, literature data give Cl 2p_{3/2} at 200.1 eV for mono-chlorinated cycles and 200.7 eV for bi-chlorinated cycles [22–24]. This indicates our samples are close to mono-chlorinated cycles but likely contains a slight Cl excess.

A previous work has demonstrated that, after annealing of PPXC thin films at 200 °C for 60 min the Cl 2p_{3/2} peak shifted from 200.8 to 200.5 eV due to the presence of oxygen at the end of the chains [8]. We have observed comparable results after 120 min of UV/O₂ treatment with a shift from 200.2 to about 200 eV of Cl 2p_{3/2}. Accordingly this is associated to the presence of O in the environment of Cl species (Fig. 6). The O 1s peak appears after 10 min of treatment and intensifies when τ is increased. The width of the O 1s peak gives evidence for at least two O species: O=C (532 eV) and O–C (533.5 eV) [25–27]. The origin of the oxygenated carbon (aromatic or aliphatic) cannot be identified at this stage [5].

The changes in the C 1s peak with the UV/O₂ treatment time give a better insight into the functionalization mechanisms. At least two species are present both for untreated films and after 10 min of UV/O₂

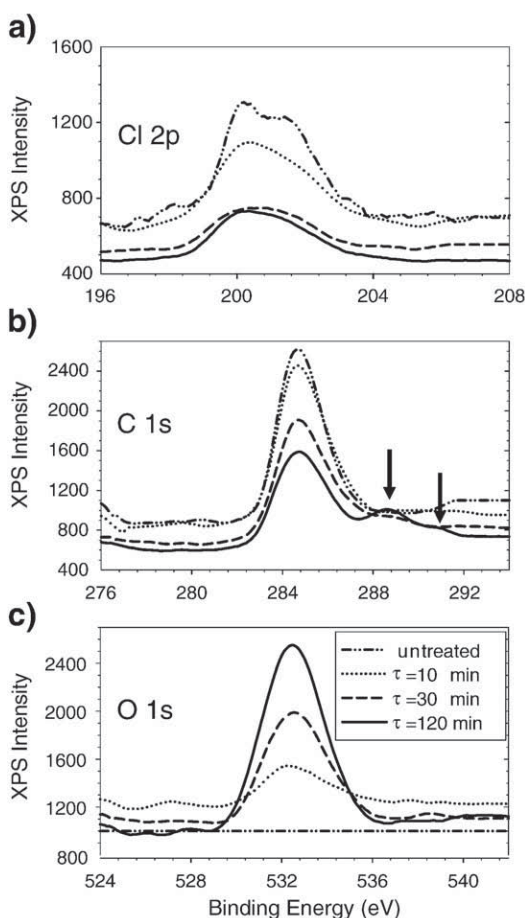


Fig. 6. High resolution XPS spectra of PPXC thin films treated under UV/O₂ atmosphere for different times: (a) Cl 2p, (b) C 1s and (c) O 1s region ($Q_T = 60$ sccm and $X_{O_2} = 0.5$). The spectra are slightly shifted along the y-axis for clarity.

Table 3

XPS binding energy (B. E.) of the chemical groups containing Cl, C and O atoms identified on the surface of functionalized parylene C thin films.

Component	Assignment	B. E. (eV)	Reference
Cl1	Cl–C (Cl 2p _{3/2})	200.0–200.2	[22–24]
Cl2	Cl–C (Cl 2p _{1/2})	201.6	[8]
C1	C–C (sp ² and sp ³)	284.7	[22]
C2	C–Cl and C–O	286–286.3	[22,28]
C3	C=O and C(O)O	287.5–288.8	[28,29]
C4	O–C(O)O	291	[30,31]
O1	O=C	532	[25,27]
O2	O–C	533.5	[25,26]

treatment. They are attributed to C–C aromatic and aliphatic bonds (284.7 eV) and to C–Cl and C–O bonding (286–286.3 eV). A third C species appears at $\tau = 30$ min corresponding to the C=O and C(O)O groups (287.5–288.8 eV). This irradiation time corresponds to a dose of about 16700 mJ/cm². It is noteworthy that the same species were found in a comparable study for an irradiation dose of 10000 mJ/cm² on PPXC and PPXN thin films [5]. A last C species O–C(O)O appears after a functionalization treatment for 120 min (C 1s binding energy found at 291 eV) [22,28–31].

Quantitative XPS analyses permits to correlate the surface composition of UV/O₂ treated samples with the theoretical chemical formula of PPXC (Fig. 7). This polymer contains one Cl atom for eight C atoms in a monomer unit, that is to say: C 89 at.% and Cl 11 at.%. The experimental XPS data give approximately for all analyses: C 85 at.% and Cl 15 at.%. This indicates the real chemical structure is not exactly mono-chlorinated but it contains a chlorine excess in agreement with the Cl 2p_{3/2} shift above-mentioned. The Fig. 7 also shows that the atomic percentage of O increases with the treatment time while C and Cl are decreasing.

3.5. Mechanisms

The UV/O₂ treatment is the most efficient to improve the hydrophilicity and the C 1s peak is the most informative to determine the structure. Consequently the variation of the four components of the C 1s peak defined in the Table 3 was analyzed as a function of the UV/O₂ treatment time (Fig. 8). The carbon C1 relative percentage decreases with the treatment time whereas C2 increases during only the first 10 min and then stays constant; C3 and C4 increase continuously.

These experimental results support the following surface functionalization mechanism: the consecutive formation of C–O bonds occurs, then aldehyde groups, carboxylic acids, and finally the carbonate OC(O)O species. Obviously these O-containing species may exist simultaneously on the surface but with relative concentration depending on the time as observed. This is also suggested by other authors [5,11]. The reaction probably results from a molecular oxygen reaction with a radical site which originates from the photolytic scission of C–H bonds from the aliphatic chain [5]. However

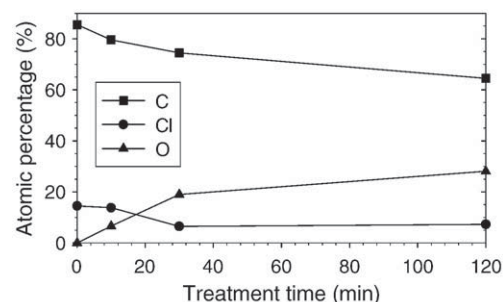


Fig. 7. Influence of the UV/O₂ treatment time on the relative composition of PPXC thin films determined by quantitative XPS analyses ($X_{O_2} = 0.5$ and $Q_T = 60$ sccm).

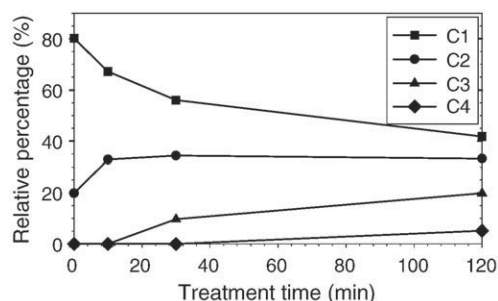


Fig. 8. Relative contribution of the various C containing components (C1, C2, C3 and C4) of UV/O₂ treated PPXC films versus the treatment time. Data were determined by deconvolution of the C 1s XPS spectra reported in Fig. 6 ($X_{O_2} = 0.5$ and $Q_T = 60$ sccm).

the participation of the ring carbons to the functionalization reactions is not clearly demonstrated since controversy exists in the literature. Bera et al. [21,32] studied parylene C and N photo-oxidation at $\lambda > 300$ nm. They predicted ring opening with formation of both aliphatic and aromatic carboxylic acids. Fortin and Lu worked on UV degradation at 254 nm of parylene and they concluded that a dose of 13 000 mJ/cm² did not really affect the IR spectrum in the ring carbons regions and so they predicted that ring opening did not occur. Nevertheless, it was demonstrated that UV irradiations at 254 nm on PPXC surfaces make possible a selective removal of the films by photolithography [11]. Photo-oxidation provokes the solubility of undesirable PPXC zones in a basic aqueous solution (as NaOH 2 wt.%). Because carboxylic acids are highly soluble in basic solutions; the fact that the insoluble PPXC films become soluble in basic solutions after UV treatments reveals the formation of carboxylic acids. This gives evidence for a preferential oxidation of the chain carbons.

Our XPS results confirm the formation of carboxylic acids with other oxygenated species but do not permit to conclude which ones from the chains or the rings are oxidized. By contrast, the IR spectra reveal oxidation of aliphatic chain and possible reactions on the aromatic cycles without ring opening.

3.6. Aging study

The knowledge of the stability of the functionalized PPXC surfaces is an important issue. Wettability measurements of the treated surfaces have been achieved after several days of aging (Fig. 9). The films treated with UV/He are quite stable independently of the treatment time. In the worst case, the contact angle changes from 40° to 44° in 10 days (efficiency loss of 10%). For the UV/O₂ treatment, which is the most efficient treatment to produce highly hydrophilic surfaces, the aging time shows some effects on the wettability value. The contact angle varies from 39° to 58° after 15 days of aging for a treatment time τ of 30 min and it changes from 5° to 8° for $\tau = 120$ min. The relatively low variation of the contact angle over a long period reveals the good stability of the functionalized films.

3.7. Influence of the film thickness

It was shown that the PPXC film thickness had an influence on the number of reactive chain endings which are present at the surface of the film [8]. It is then possible that the thickness has an effect on the functionalization treatments. Film thicknesses ranging from 300 to 1630 nm were treated under UV/O₂ ($Q_T = 60$ sccm; $X_{O_2} = 0.5$), UV/He and UV/air. The treatment time was in any cases 120 min. For all treatments, the contact angle was found independent on the films thickness.

Transmission FTIR spectra of UV/O₂ treated films (deposited on silica substrates) show an increasing of the C=O (1710 cm^{-1}) peak relative intensity with the increasing of the film thickness. But, for the UV/He treatment, the C=O peak intensity is very low as expected for

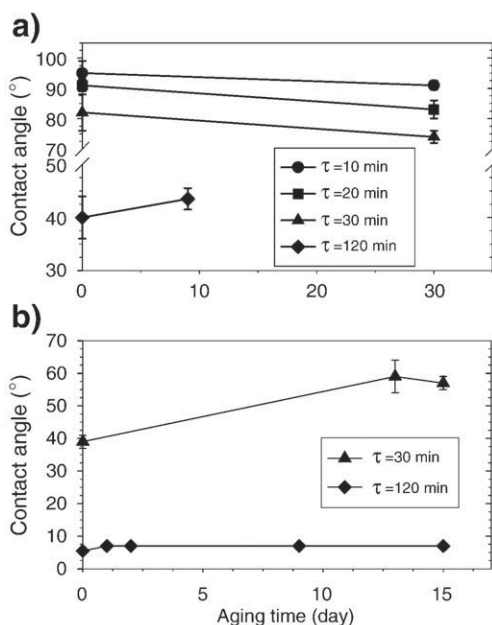


Fig. 9. Influence of aging on the wettability (water droplets) of functionalized PPXC thin films. The PPXC surfaces were treated by (a) UV/He (treatment time $\tau = 10, 20, 30$ and 120 min; $Q_T = 44$ sccm) and (b) UV/O₂ ($\tau = 30$ and 120 min; $X_{O_2} = 0.5$; $Q_T = 60$ and 240 sccm).

this treatment under inert gas and it stays quite constant. These analyses confirm that the UV/O₂ functionalization process affects both the surface and the bulk of the film. As mentioned above, the mechanism in the bulk is induced by photolytic scission due to the depth penetration of photons. The fact that C=O relative intensity is increasing with the film thickness gives evidence for diffusion of oxygen species from the reactive atmosphere.

To complete these data UV-Vis spectrophotometry analyses were realized on samples deposited on glass substrates. For the UV/O₂, UV/air and UV/He treatments the film thickness has no influence on the transmittance in the visible range, e.g. 470 nm (Fig. 10). The transmittance remains high near the average value of 90%. However the effect of the treatments is significant in the UV domain. Indeed, in the absorption edge region, e.g. at 340 nm, the transmittance is independent on the thickness for as-deposited thin films, as observed in the visible range. This means that the wavelength 340 nm is just above the absorption threshold of parylene C films and consequently it does not follow the Beer-Lambert law. However the transmittance at this wavelength decreases when the thickness increases for the UV/O₂, UV/air and UV/He treatments as shown by the Fig. 11. This clearly confirms a bulk mechanism induced by UV irradiation of the films.

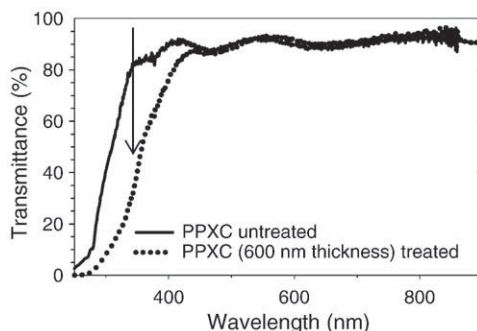


Fig. 10. UV-Vis transmittance spectra of as-deposited (untreated) and UV/O₂ treated PPXC films grown on glass substrate with a thickness of 600 nm (the treatment conditions were $Q_T = 60$ sccm, $X_{O_2} = 0.5$ for 120 min). The arrow points the wavelength 340 nm.

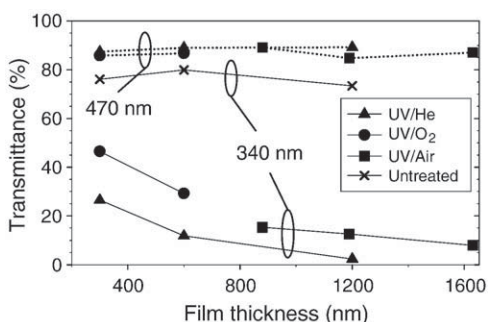


Fig. 11. Variation of the transmittance at 340 and 470 nm of PPXC thin films deposited on glass substrate versus the films thickness for untreated sample and different surface treatments. The treatment time was constant for all treatments (120 min).

4. Conclusions

This work aimed to study different functionalization treatments of Parylene C surface by UV irradiation at 254 nm under various reactive gas atmospheres. The goal was to develop long life efficient treatments, compatible with CVD processes, to improve the hydrophilicity without altering the optical properties of the thin films. Whatever the reactive gas atmosphere (H_2O_2 , H_2O , O_2 , air and He) the presence of UV was required to modify the surface. The UV/ O_2 treatment exhibits the best efficiency; it permits to decrease the water from about 100° to 6° by keeping an excellent transparency in the visible range. So, the hydrophobic surface of parylene C can be switched to highly hydrophilic by this dry method. Moreover, the UV/ O_2 functionalized films have been aged several days under ambient atmosphere and a variation of maximum 20% of the water contact angle was found after 15 days. This reveals the good stability of the modified PPXC surface.

The mechanism of surface functionalization has been investigated. Aldehydes, carboxylic acids and carbonates are the main species formed. Oxidation reactions occur essentially in the aliphatic chain. The aromatic cycles are likely involved but without ring opening. The influence of the thickness of PPXC films on the treatment efficiency supports the assumption of a dual mechanism: (i) a surface photo-oxidation with oxidizing atmospheres and (ii) bulk photolytic reactions involving O species diffusing from the external surface.

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