

HYDROPHILIC FLUOROCARBON COATINGS VIA PLASMA ENHANCED-CHEMICAL VAPOUR CO-DEPOSITION OF ACRYLIC ACID AND HEXAFLUOROPROPYLENE OXIDE

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Abstract

The co-deposition of acrylic acid and hexafluoropropylene oxide in pulsed plasmas was studied with the purpose to obtain wettable fluorocarbon coatings containing carboxylic acid groups, which are potentially useful for several employments, e.g., as proton-exchange membranes for electrochemical applications.

It was found that the hydrophilic fluorocarbon thin films with the higher concentration of surface acidic groups can be obtained at lower duty cycle. After one week of immersion in water at 80°C the trends are inverted, the concentration of acidic groups and the wettability increase with the duty cycle.

Keywords and phrases: plasma enhanced-chemical vapour deposition, hydrophilic fluorocarbon coatings, pulsed plasmas, water stability.

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1. Introduction

Hydrophilic fluorocarbon coatings attract significant attention for their potential applications, such as membranes for electrochemical devices (e.g., proton-exchange membrane for fuel cells, PEMGCs) [1], where suitable electrical properties and high stability under very harsh media are required [1].

Common fluoropolymers, e.g., polytetrafluoroethylene (PTFE), despite their unique properties such as high thermal stability, excellent chemical resistance, low friction coefficient, low dielectric constant, superior weatherability, etc. [2-9], are unsuitable for such applications for their hydrophobic nature and absence of ionic conductivity. For this reason, processes able to produce hydrophilic and ion conductive fluoropolymers would be desirable. Radiation grafting was used for many years for this purpose on several fluoropolymers [1, 10-12]. This process basically consists in irradiating the fluoropolymer with high-energy photons in the presence of a monomer, e.g., acrylic acid (AA) [1], which is then grafted onto the polymer forming a hydrophilic surface, while preserving the other fluoropolymer properties.

In this paper, we describe a different approach to obtain thin, hydrophilic, fluorocarbon coatings containing acid groups, by means of the co-polymerization of hexafluoropropylene oxide (C_3F_6O) and acrylic acid with plasma enhanced-chemical vapour deposition (PE-CVD). This is a single step process allowing the deposition, on a wide range of substrates, of thin films with controlled composition, thickness, morphology, and hydrophilicity [13]. Like all the PE-CVD processes, the proposed approach has several advantages, e.g., it is solvent free and eco-friendly, it allows the deposition of strongly adhered pinhole-free polymer films on different substrates with several geometries or shapes, the treatment is performed at low temperature with minimal thermal stress, resistance to degradation and with the possibility to treat also thermolabile materials (e.g., paper, polymers, etc.) [14-20]. At the best of

our knowledge, the co-deposition by PE-CVD of fluorocarbon and a carboxylic acid for the preparation of hydrophilic fluorinated polymer has never been reported. So far published works, in fact, deal with the copolymerization of acrylic acid with volatile hydrocarbons (e.g., styrene [13]) not fluorocarbons.

2. Material and Methods

The experiments were carried out in a stainless steel, parallel plate, low pressure plasma reactor consisting of a cylindrical stainless steel chamber (internal diameter, 200mm) with two stainless steel electrodes (inter-electrode distance, 40mm). The upper electrode (diameter, 170mm) was connected to a 13.56MHz radio frequency (RF)-power supply through an automatic L-type matching network unit, while the lower electrode (diameter, 150mm), on which the samples were positioned during the deposition, was grounded. The flow rate of gases was controlled by means of mass flow controllers (*MKS Instruments*), while the acrylic acid vapour flow rate was regulated with a needle valve. The reactor was pumped by a turbomolecular-rotary pumping system, while, the pressure was measured and controlled with a baratron gauge and a manual throttle valve, respectively.

The experiments were conducted at 13.33Pa, with the gas feed composed by 10sccm (standard cubic centimeters per minute) of Ar (*Rivoira*, purity > 99.9%), 10sccm of C₃F₆O (*Sigma Aldrich*, purity 98%), and 6sccm of acrylic acid (*Sigma Aldrich*, purity 99%). The input power, fixed at 80W, was modulated with a period of 100ms and duty cycles (DC) between 10 and 100%. Films obtained from pure acrylic acid (6sccm) or pure hexafluoropropylene oxide (6sccm) at DC value of 10% were also deposited for comparison.

The depositions were performed on polished c-Si(100) wafers (*Microchemicals*) for X-ray photoelectron spectroscopy (XPS) analyses, water contact angle (WCA), and deposition rate (Rd) evaluation. Teflon discs (*Goodfellow*, diameter, 15mm) were utilized to study the water

resistance and for toluidine blue O (TBO) test, while Solupor® 16P05A (ultra high molecular weight polyethylene film, 10g/m^2) was employed for electrochemical impedance spectroscopy (EIS) measurements.

All substrates were prior sonicated, for 15 minutes, in ethanol.

(i) XPS analyses

The surface chemical composition was carried out by means of XPS using a Theta Probe spectrometer (*Thermo Scientific*) equipped with a monochromatic Al K_{α} X-ray source (1486.6eV) operated at 15KV and a spot size of $300\mu\text{m}$, corresponding to a power of 70W. Survey (0-1200eV) and high resolution (C1s, O1s, F1s) spectra were recorded in FAT (fixed analyzer transmission) mode at pass energy of 200eV and 100eV, respectively. All spectra were acquired at a take-off angle of 37° with respect to the sample surface. A flood gun was used to balance the surface charging. The C1s signal for the hydrocarbon component (285.0eV) was used as internal standard for charging correction. Atomic percentages were calculated from the high resolution spectra using the Scofield sensitivity factors set in the XPS data processing software (Avantage 4.87) and a non-linear Shirley background subtraction algorithm.

Measurements, performed on repeated samples, allowed to register a maximum relative standard deviation (RSD) of about 6%. The same processing software was employed for the best-fitting procedure of the C1s signals.

(ii) WCA measurements

Sessile drop water contact angle values were measured with a manual goniometer (*Ramé.Hart, Inc.*), utilizing a $2\mu\text{l}$ water drop. The measurements were performed immediately after the deposition process, after 30 days of air exposure and after 7 days of water immersion at 80°C .

The static WCA values were averaged over 5 measurements on each sample.

(iii) Deposition rate

The deposition rate (Rd) was estimated by thickness measurements realized with a stylus profiler (*KLA-Tencor AlphaStep® D-120*) on films deposited on c-Si(100) substrates.

All values reported in this article are the average of five measurements.

(iv) EIS measurements

About 1µm thick coatings were deposited onto 16P05A Solupor® membrane and proton conductivity was measured in the film plane by electrochemical impedance spectroscopy (EIS). Two-point probe measurements on the membrane samples were conducted in a custom-built probe cell with a distance of 3.50cm between the platinum-wire electrodes. The cell was run in a potentiostatic mode by applying a sinusoidal AC potential around a DC potential (equipment: Bio-Logic SP-150) of 0.5V. The amplitude of the superposed AC potential was 10mV, the frequency was varied from 1MHz to 100Hz, with 74 points per decade and with an averaging of 5 measured values for each sampled point.

(v) Toluidine blue O (TBO) test

The surface concentration of the carboxylic groups, before and after water immersion at 80°C, was determined by TBO test [21], utilizing a calibration curve produced by measuring, with a UV/VIS 6505 G/ACC spectrophotometer (*Perkin Elmer*), the absorbance at 633nm of TBO solutions of known concentration. The test was performed by immersing the substrate in 20ml of a 5×10^{-4} M TBO aqueous solution at pH 10 (for NaOH). The formation of ionic complexes between the carboxylic groups on the coatings and the cationic dye was allowed to proceed for 5h at 30°C. The substrates were then rinsed with NaOH 0.01M, to remove the unbound TBO molecules, than incubated in 3ml of 50% v/v acetic acid (1min, vortex) in order to separate the complexed TBO from the surface of the coatings. The surface density of COOH groups was calculated from the absorbance of the desorbed dye solution at 633nm, for comparison

with the calibration curve. It was assumed that 1mol of TBO adsorbed by the substrate and than desorbed in acetic acid corresponds to 1mol of COOH functionalities on the coating [22].

3. Results and Discussion

The XPS atomic concentrations and the WCA values of the as-deposited films obtained at different duty cycle values are reported in Table 1, along with their deposition rates.

Table 1. XPS atomic composition, WCA values of as-deposited coatings and Rd values, as a function of the DC applied during the plasma processes

DC (%)	C (%)	O (%)	F (%)	WCA (°)	Rd (nm/min)
10	60 ± 6	15 ± 2	25 ± 3	55 ± 2	4.2 ± 0.5
50	49 ± 4	9 ± 2	42 ± 4	64 ± 3	5.6 ± 0.4
80	50 ± 6	9 ± 3	41 ± 2	71 ± 2	10.0 ± 0.6
100	49 ± 3	11 ± 2	40 ± 3	83 ± 2	10.8 ± 0.5

The XPS results indicate that oxygen is included in all the deposits, the highest concentration being 15% is shown for DC 10%, the mildest condition which also presents the lowest amount of fluorine (25%). The best fitting of the C1s spectra (Figure 1) are reported in Table 2; the fitting were accomplished with the peaks listed in Table 3 [23, 24].

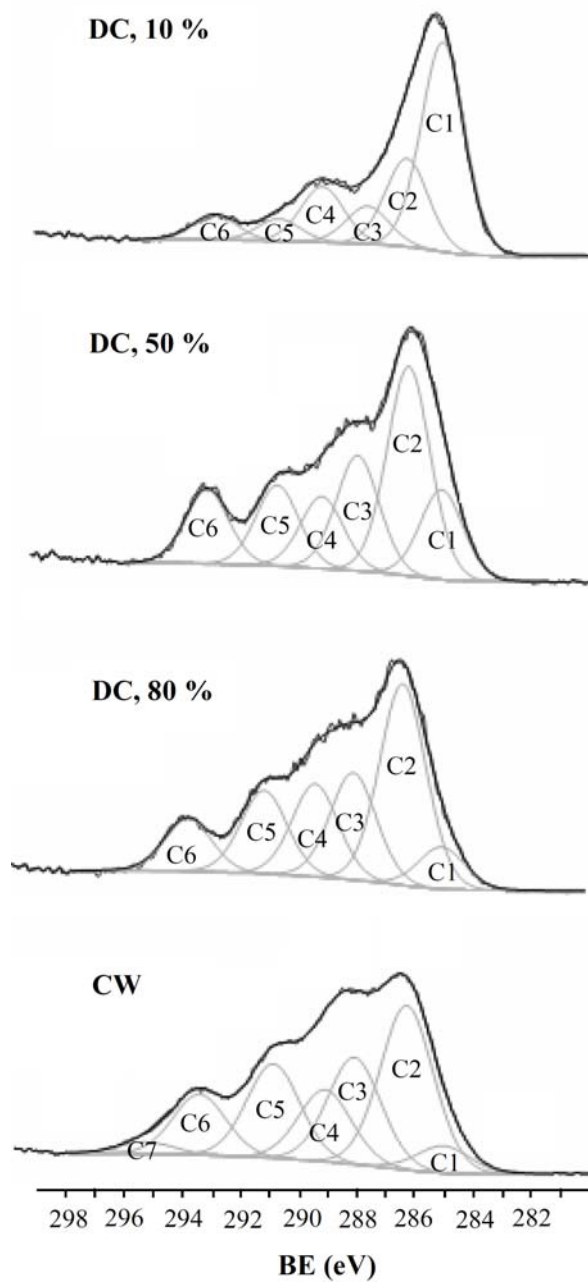


Figure 1. High resolution XPS C1s spectra of the coatings deposited at different DC value, immediately after the end of the deposition process.

Table 2. XPS C1s spectra fitting results

C1s components	DC 10%	DC 50%	DC 80%	DC 100%
C1 (285.0eV)	34.8 ± 0.5	7.0 ± 0.2	9.2 ± 0.4	5.9 ± 0.2
C2 (286.1 ± 0.1eV)	19.9 ± 0.3	30.0 ± 0.2	28.0 ± 0.3	24.3 ± 0.5
C3 (287.7 ± 0.4eV)	15.8 ± 0.3	20.5 ± 0.3	19.0 ± 0.3	17.8 ± 0.3
C4 (289.4 ± 0.4eV)	16.6 ± 0.2	17.5 ± 0.2	17.8 ± 0.3	14.7 ± 0.2
C5 (290.6 ± 0.2eV)	6.3 ± 0.2	16.7 ± 0.3	16.1 ± 0.2	18.6 ± 0.2
C6 (293.0 ± 0.2eV)	6.6 ± 0.2	8.3 ± 0.5	15.1 ± 0.4	15.4 ± 0.2
C7 (294.7 ± 0.3eV)	/	/	/	3.6 ± 0.4

Table 3. Components utilized for the fitting of C1s spectra

Peak	BE (eV)	Chemical groups
C1	285.0	C-C, C-H
C2	286.1 ± 0.1	<u>C</u> -CF ₂ , C-O, <u>C</u> -CF
C3	287.7 ± 0.4	<u>C</u> -CF ₃ , C=O, O-C-O, C(O)O- <u>CH</u> ₂ -CF ₃
C4	289.4 ± 0.4	O-C=O,CF
C5	290.6 ± 0.2	<u>CF</u> ₂ -CH ₂ , C(O)O- <u>CF</u> ₂ -CH ₂
C6	293.0 ± 0.2	<u>CF</u> ₃ -C(O)O, <u>CF</u> ₃ -CH ₂ -C(O)O
C7	294.7 ± 0.3	<u>CF</u> ₃ -O

The component C7, at 294.7eV, is detected only in continuous mode. The peak is assigned to CF₃-O and can be due to the more complex chemical environment (higher disorder) of the film obtained in continuous mode [25-27]. The more complex chemical environment also causes peak broadening, since the full width at half maximum (FWHM) utilized for the fitting increases from 1.8eV to 2.3eV, as duty cycle is varied from 10% to 100%. More specifically, the FWHM is 1.8eV at DC 10%, 1.9eV at DC 50%, 2.1eV at DC 80%, and 2.3eV at DC 100%.

In order to quantify the carboxyl acidic groups, which are characterized by a peak that in the C1s XPS signal overlaps with that of esters and CF groups (peak C4 in Table 4), it was conducted the TBO test

which is specific for the carboxylic acid groups. The results, reported in Figure 2, show that the amount of acidic groups in the coating is maximum at the lowest duty cycle value, i.e., in mild deposition conditions, when the XPS oxygen concentration is maximum.

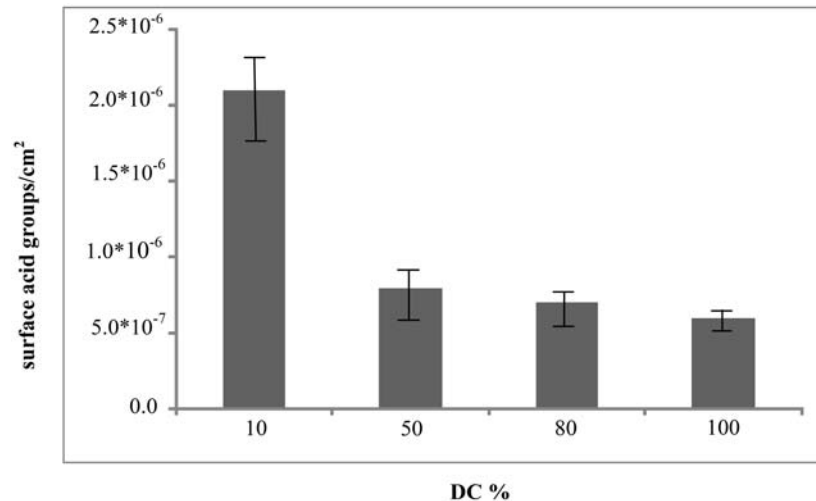


Figure 2. TBO test results. Surface acid groups concentration for coatings deposited at different values of DC. The test were performed immediately after the end of the deposition process. Films thickness about 100nm.

The reduction of carboxylic acidic groups with increasing the duty cycle can be due to the higher fragmentation of acrylic acid, with consequent reduction of the carboxylic groups available to be incorporated in the growing polymer which also results characterized by a higher cross-linking, as it can be easily appreciated by the fitting results of Figure 1.

The results of Figure 2 are in agreement with the WCA measurements of Table 1. The sample deposited at DC 10%, characterized by the highest content of carboxylic groups, is expected to be the most hydrophilic and, in fact, it is characterized by the lowest water contact angle value. The WCA values of Table 1 are higher than typical surfaces containing carboxylic groups for the contemporaneous presence of fluorine atoms, which make the surface less hydrophilic. A

coating deposited in plasma fed only with acrylic acid (without fluorine) at DC 10%, in fact, showed a WCA value of $17^\circ \pm 3^\circ$, while for a coating deposited from pure hexafluoropropylene oxide (no acrylic acid) the registered WCA value was $120^\circ \pm 5^\circ$.

The XPS oxygen and fluorine atomic concentration, the WCA values and the concentration of carboxylic acidic group obtained at different DC are compared in Figure 3, immediately after the end of the deposition process and after 7 days of immersion in water at 80°C . It was decided to study the hot water behaviour of the as deposited films, because it was observed that the storage in air does not significantly influence the surface hydrophilicity of the coatings, in fact, samples as deposited and air-aged for 30 days showed, substantially, the same WCA values, as reported in Figure 4.

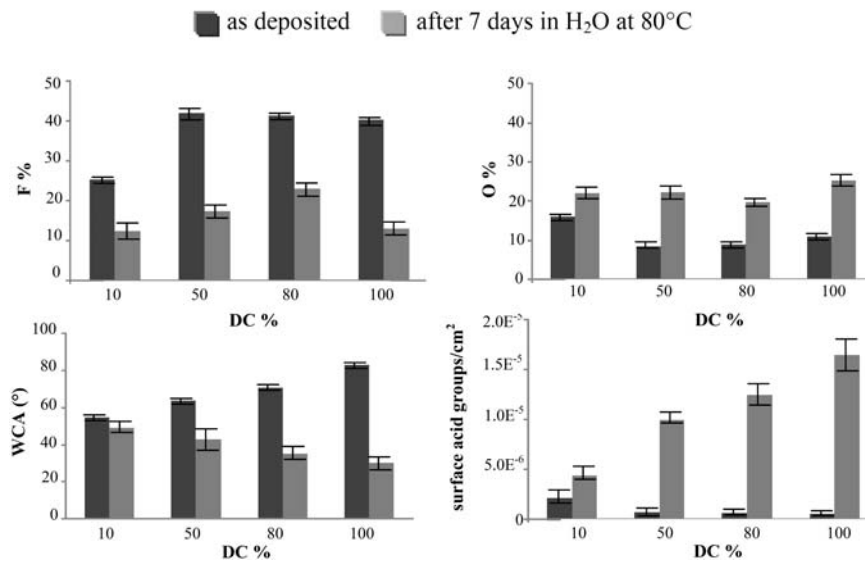


Figure 3. Fluorine and oxygen concentrations, WCA value and surface acidic group concentration, before and after 7 days of water immersion at 80°C .

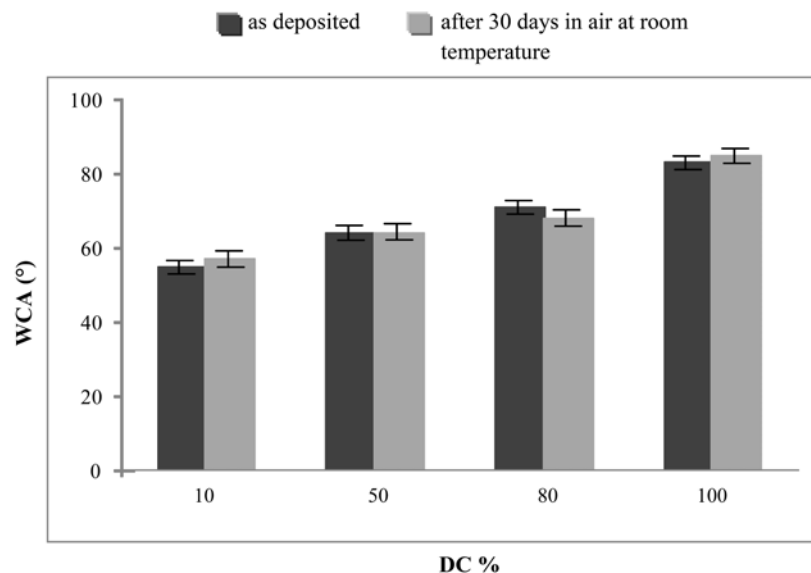


Figure 4. WCA value before and after 30 days of air exposure at room temperature.

Observing Figure 3, it can be appreciated that the immersion in water affects the fluorine and oxygen content, reduces the WCA and increases the concentration of acidic groups. Moreover, while in the as-deposited film the concentration of acidic groups decreases with DC, after the immersion in water, there is an inversion of trend. The higher concentration is registered for 100% DC. The raise in the concentration of carboxylic groups after water immersion is reasonably due to a swollen of the coating which increases the number of the acid groups probed in the bulk with respect to the surface. This effect is particularly evident for samples deposited at higher duty cycle value and in continuous wave mode, probably because it is associated to hydrolyzing reactions, promoted by water and high temperature, of the esteric groups, which are more plentiful at higher duty cycle and in continuous mode, due to the higher precursor fragmentation [28]. The concentration of acidic groups as well as the water contact angle do not change for further water immersion and remain stable also after 1 month of ageing in air at room temperature.

Preliminary EIS measurements have been, finally, carried out to test specific proton conductivity of deposited films for their possible future utilization in electrochemical devices, e.g., as proton-exchange membrane for fuel cells [1].

Results collected in Table 4 show proton conductivities in the range 13-23mS/cm. Though these values are low when compared to proton conductivity of Nafion® (104mS/cm), they are quite promising with respect to many of the results reported in literature on the plasma deposition of proton conductive membranes [29].

Table 4. Specific proton conductivity (σ) values of as deposited coatings, after 1 hour of water immersion at 80°C and dried at 40°C overnight, as a function of the DC applied during the plasma processes

DC (%)	σ (mS/cm)
10	20 ± 4
50	15 ± 3
80	23 ± 5
100	16 ± 1

4. Conclusion

In this paper, we have shown that it is possible to deposit fluorine containing thin films with acidic carboxylic groups and hydrophilic behaviour by plasma enhanced chemical vapour deposition from acrylic acid and hexafluoropropylene oxide mixtures, utilizing Ar as carrier gas.

As deposited coating, obtained with low DC, i.e., low plasma fragmentation, showed the higher acid groups concentration and, therefore, the best hydrophilic character.

The immersion in water at 80°C affects the concentration of oxygen and fluorine and the carboxylic acidic groups amount. After the immersion in water the concentration of acidic groups increases with the duty cycle value.

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