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Role of the surface chemistry of plasma-polymer layers on their long-term anti-fogging behavior

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Abstract

Long-term anti-fogging capability of plasma-coatings obtained from hydrophilic precursor, such as 2-(dimethylamino)ethyl methacrylate or acrylic acid, and hydrophobic monomer, 1H,1H,2H-perfluoro-1-decene, deposited on polycarbonate is studied for two different aging. These films, when freshly prepared, show simultaneous hydrophilicity / oleophobicity for HDFD concentrations < 50 %. They fulfill anti-fogging criteria: low water contact angle (< 20°), high hexadecane contact angle around 70° and preservation of optical transparency after water vapor contact. Depending on their chemical structure, only p-AA-co-HDFD with 20 - 40 % of HDFD retain their anti-fogging properties after a thermal aging while all of them are altered when dipped in hot water. p-AA-co-HDFD is more efficient than p-DAME-co-HDFD reducing airborne contamination and improving the long-term anti-fogging performance.

Key words: plasma co-deposition; hydrophilic / oleophobic; anti-fogging; wetting; aging.

I. Introduction

Anti-fogging property is defined as the ability to avoid condensation of water vapor onto material surface at ambient atmosphere saturated of humidity, so-called fog that restricts the light transmission. [1-3] Elaboration of anti-fogging surfaces which induces the growth of an uniform water thin film rather than droplets' condensation was studied for various applications. [4-7] Prevention of fog formation by controlling the surface wettability can be reached with hydrophilic surface since such a surface has high surface free energy and therefore, is able to promote droplets' spreading. However, this type of anti-fogging surface can be easily contaminated by the airborne hydrocarbon present at ambient air leading to its hydrophilicity disappearance. [8-9] In order to improve the long-term anti-fogging properties, two main solutions are proposed.

The first one involves superhydrophilic coatings which can be organic or inorganic ones. [10-13] However, the inorganic superhydrophilic coatings have shown better long-term anti-fogging property than the organic ones. Indeed, the poly(ethylene terephthalate) (PET) treated by dioxygen plasma and indium tin oxide (In_2O_3-SnO_2)-coated glasses (ITO) treated by an electrochemical method were prepared as organic and inorganic superhydrophilic surfaces, respectively, with WCA (water contact angle) nearly zero. After 7 days, an increase of WCA to 40° on PET surface and to only 18° on ITO glass was observed. [12] One of the more stable superhydrophilic inorganic surfaces is the hierarchical nanoporous layer of silicate glass etched by an alkaline solution with a WCA at about 5° for more than one year. [14] In the case of superhydrophilic organic thin coating, the polydiethylene glycol bis(allyl carbonate) treated by Ar ions implantation under dioxygen partial pressure can retain its anti-fogging property during only the first 2000 h to attain a WCA ≅ 40°. [8]

On the other hand, in order to preserve hydrophilicity of the surface from organic contamination, oil-repellent or oleophobic properties are requested. Thus, the second type of long-term anti-fogging surface is based on coatings with simultaneous hydrophilic / oleophobic properties. Such a surface is generally grafted by hydrophilic polymers and fluorinated surfactants, thus the hydrophilic perfluorinated copolymers and perfluopolyether polymers are good candidates for this type of surface. [15-17] But until now, it is rare to find a report describing long-term anti-fogging capability of such a surface. In our knowledge, just only one study on different perfluoropolyethers (PFPE) showed that the anti-fogging properties are retained after 14 aging days with ($HOCH_2CF_2O$-$[CF_2CF_2O]_m$-$[CF_2O]_n$-CF_2CH_2OH) coating whose hexadecane contact angle (HCA) = 70.1 ± 0.9°, whereas another type of PFPE (CF_3CF_2O-$[CF_2CF_2O]_m$-$[CF_2O]_n$-CF_2CF_3) with lower oleophobocity (HCA = 32.6 ± 0.5°) is not anti-fogging. [17] Moreover, no explanation is given for such a behavior.

This work focuses on the long-term anti-fogging properties of hydrophilic / oleophobic coatings, deposited thanks to the pulsed-plasma polymerization technique. These coatings are elaborated from mixture of 2-(dimethylamino)ethyl methacrylate (DAME) or acrylic acid (AA) used as hydrophilic monomer and 1H,1H,2H-perfluoro-1-decene (HDFD) as hydrophobic monomer. [18] Plasma-deposited fluorocarbon films are known to rearrange and to be oxidized after elaboration. Surface rearrangement of the polymeric chains is frequently investigated by air / water contact angles measurement [19,20] whereas post-oxidation due to free radicals in the plasma coatings, by X-ray photoelectron spectroscopy (XPS). [21-23] Thus, in this study, thermal stability and wet surrounding resistance of hydrophilic / oleophobic plasma films deposited on polycarbonate (PC) substrates are carried out by wettability measurements and XPS analysis. The anti-fogging properties of aged surfaces are also examined by water vapor contact test.

II. Experimental part

II.1. Elaboration of p-DAME-co-HDFD and p-AA-co-HDFD coatings

All the chemical products were used without any purification. 2-(dimethylamino) ethyl methacrylate (DAME, $CH_2=C(CH_3)COOCH_2CH_2N(CH_3)_2$, 99 % purity) was purchased from Acros Organics (France) while acrylic acid (AA, $CH_2=CHCOOH$, 99 % purity) and 1H,1H,2H-perfluoro-1-decene (HDFD, $CF_3(CH_2)_7CH=CH_2$, 99 % purity) were purchased from Sigma Aldrich (France).

Plasma polymerization process was carried out with a capacitively coupled RF (13.56 MHz) reactor (MG300S, Plassys). Substrates were located on the lower cathode in cylindrical aluminum chamber (28 cm diameter and 6.15 L volume) with two parallel circular electrodes (20 cm diameter with 12.8 cm gap). The argon gas and precursor vapors (DAME, AA, HDFD) were injected through an electrode-integrated shower above the reaction chamber. To improve adhesion of the polymer layers on the substrate, the latter was pre-treated by Ar plasma (discharge power P = 100 W, flow Fl = 10 sccm, duration t = 30 s). The first precursor was then injected until required partial pressure was attained. The second one was then added to obtain total pressure (p) of 0.02 Torr. The pressure was controlled by a Baratron gauge. p-DAME-co-HDFD and p-AA-co-HDFD coatings with different % HDFD and deposition times (Table 1) were deposited using the pulsed plasma technique with a discharge power P = 10 W. The pulse on-time (t_{on}) and pulse off-time (t_{off}) were 17 µs and 150 µs, respectively, which correspond to an applied frequency f = 6 kHz and a duty cycle $d.c.$ (defined as the ratio of pulse on-time to period) = 10 %.

Table 1. p-DAME-co-HDFD and p-AA-co-HDFD at different HDFD proportions (%) and deposition times with % F and F / C, O / C ratios of fresh coatings determined by XPS analyses.

	HDFD (%)	Deposition time (min)	Sample	F / C	O / C	F (%)	Film thickness (nm)
p-DAME-co-HDFD	10	10	D1	0.22	0.21	14.4	58.2
	20		D2	0.34	0.18	21.4	37.7
	30		D3	0.34	0.19	21.3	n-meas
	40		D4	0.36	0.22	21.7	n-meas
	50		D5	0.42	0.19	25.1	14.2
	20	20	D6	0.33	0.19	20.8	55.4
		30	D7	0.38	0.17	23.5	72.2
p-AA-co-HDFD	10	10	A1	0.40	0.43	22.0	68.4
	20		A2	0.42	0.41	22.8	38.6
	30		A3	0.54	0.34	28.5	n-meas
	40		A4	0.54	0.36	28.4	n-meas
	50		A5	0.54	0.36	28.3	15.6
	50	30	A6	0.67	0.28	34.3	103.3

n-meas : not measured

II.2. Film characterization

X-Ray Photoelectron Spectroscopy (XPS)

Plasma codeposits onto PC substrate were analyzed by XPS instrument (Kratos Axis Nova, UK at the Institut des Matériaux de Nantes, France) with a monochromatic Al Kα beam. The core-level signals were obtained at electron emission take-off angle of 90° relative to the sample surface. The curve fitting was achieved using CasaXPS software with a constant value of the full width at half-maximum (FWHM) for the Gaussian peaks for all atomic components. The quantification was determined from high resolution peak area ratios and was reliable to ± 5 %. Since the XPS are run one day after the plasma-deposition, all samples are kept under vacuum prior to their analysis.

Layer thickness measurement

Thickness measurement of the different layers deposited on Si/SiO_2 wafers was done thanks to atomic force microscopy (AFM, Bruker Innova). Before deposition, the substrate was partially masked. After deposition, the mask was removed and the created step was

representative of the deposit thickness. Images (50 x 50 µm^2) were scanned in tapping mode at ambient air. The film thickness was determined using the Gwyddion software.

Wettability measurement

Static contact angle measurements of extremely pure water (WCA) (MilliQ Water System, resistivity 18 MΩ cm^{-1}) and n-hexadecane droplets (HCA) ($CH_3(CH_2)_{14}CH_3$, Sigma-Aldrich France, ≥ 99 %) on the just-prepared plasma layers were carried out thanks a goniometer with 3 µL of liquid. For each reported contact angle, ten values taken on both sides of five drops were averaged.

II.3. Anti-fogging characterization

Anti-fogging properties of thin films were measured as described in the ISO standard EN 168 protocol. [19] The sample was maintained 5 cm over hot water at 60°C for 1 min then, the water condensation was defined as “fogging” or “slightly fogging” or “anti-fogging” (Figure 1).

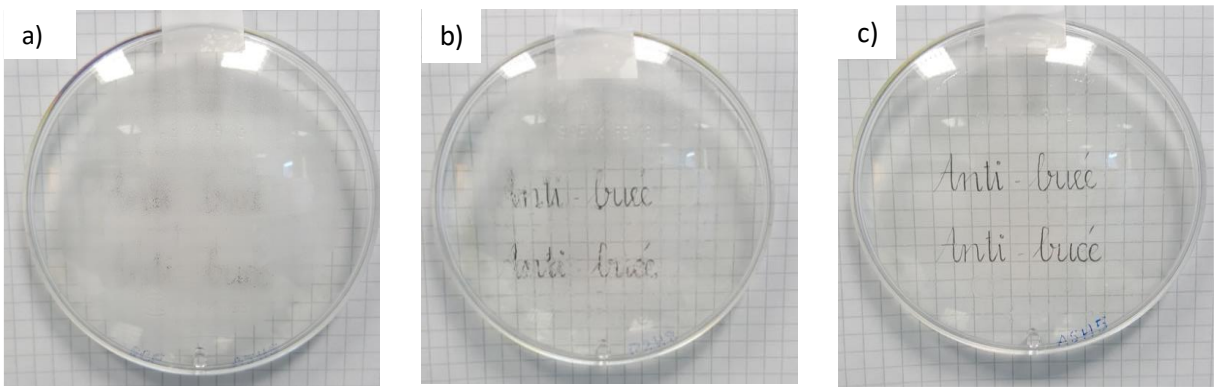

Figure 1. Illustration of a) “fogging” or b) “slightly fogging” or c) “anti-fogging” surface exposed 1 min to water vapor.

II.4. Anti-fogging plasma codeposits aging

Coated PC was aged by two different processes. The first one (so-called 5CF) was based on a thermal effect at humid atmosphere while the second was associated to the wet surrounding

(so-called WS) in order to study stability of the anti-fogging property as well as the film transmittance. Concerning the 5CF aging, the sample was exposed to 5 cycles of different durations, temperatures and relative humidity [(16 h at 85°C and 95 % of humidity) - (3 h at -20°C and 75 % of humidity) - (6 h at 85°C and 5 % of humidity)]. For the WS aging, the films were immersed in water at 60°C during 10 days.

After such an aging, the coated PC was stored in ambient environment for 24 h then, the anti-fogging property was measured as described in the previous paragraph.

III. RESULTS AND DISCUSSION

p-DAME-co-HDFD and p-AA-co-HDFD thin films are deposited by low pressure plasma method with different HDFD proportions in the plasma phase (10 - 50 %) and various durations (i.e. thicknesses). Whatever the plasma conditions are, the fresh coatings show hydrophilic - oleophobic properties with low WCA (around or less than 20°) and HCA value in the range of 52° to 70°. We also noticed that p-AA-co-HDFD (WCA < 5°, HCA = 64° - 70°) co-deposits are more hydrophilic and more oleophobic than p-DAME-co-HDFD films (WCA = 5 - 20°, HCA = 52° - 64°). These coatings show then anti-fogging properties where PC transparency is preserved through the formation of a continuous water film after water vapor contact (Figure 1c).

In order to study stability and durability of their anti-fogging properties, different synthesized layers are aged according to the two processes: 5CF (thermal effect) and WS (wet surrounding) then their anti-fogging properties are analyzed by wettability and transmittance measurements.

III.1. Evolution of contact angles of the polymeric layers after aging

After 5CF aging, water contact angle (WCA) of aged p-DAME-co-HDFD increases slightly (except D6) and reaches almost the same value of around 25.7° - 29.7° (Figure 2) whatever the initial surface chemistry. In a different manner, hydrophilicity of the aged p-AA-co-HDFD appears to be less altered since WCA is only increased for samples bearing high amount of fluorinated groups. The obtained value of WCA around 26.9° for the aged p-AA-co-HDFD (50 % HDFD) is close to that of aged p-DAME-co-HDFD. Beside this hydrophilicity alteration of both aged polymers, their HCA value does not significantly change whatever their surface chemistry; their oleophobic character is then preserved after such a thermal aging. Since WCA remains lower than 40° and HCA is around 60° - 70°, all these aged surfaces are still hydrophilic / oleophobic even if they are less hydrophilic compared to fresh ones. The small hydrophobicity increase could be due to the rearrangement of hydrophobic segments (so-called "hydrophobic recovery") in the film [24-26], the cross-linking of radicals remained in fresh plasma films, the contamination of airborne hydrocarbon or the exsudation of additives from PC substrate. Moreover, previous studies on poly(perfluorocarbon) reported that perfluoroalkyl groups with a low surface free energy could move to the surface during the aging at room temperature. [27,28] Li *et al.* [29] showed that heating polymer layers promotes the motion of fluorinated chains towards air - polymer interface in order to minimize surface free energy of the layer. In the aging process of our films, the temperature raises to 85°C enhancing the chain mobility and increasing the disorder of the bulk polymer. This phenomenon is exacerbated by plasticizing effect of absorbed water due to humid surrounding atmosphere (relative humidity of 20 %) and by the hydrophilic character of the layer. [12] Indeed, the absorbed water molecules may increase the free volume of polymeric film and thus may favor the chain turn-over. As a result, the perfluorocarbon groups may easily move towards material surface, leading to the observed aging effect. This mobility is all the more favored that plasma polymers are known as amorphous films. However, the plasticization due to absorbed water is controversial as

described in [30], where the motion of polyurethane segments of fluorinated poly(amide urethane) is less important than that of fluorinated chains.

Besides, the hydrophilicity decrease of p-DAME-co-HDFD samples is independent on the fluorinated segments proportion in plasma phase whereas the p-AA-co-HDFD layers only age at a threshold plasma-concentration of HDFD (around 50 %). Their different behavior towards thermal aging could be explained either by flexibility of hydrophilic segment or by contamination resistance of the fluorinated chains (which will be discussed in XPS part). As described in [31,32], the incorporation of a polar group, such as amine one in DAME monomer, induces the formation of intermolecular hydrogen bonds that strongly reinforce the interactions between side chains and makes DAME main chains more rigid than AA main ones. Thus, any local or long distance motion towards the surface will be mostly promoted by the fluorinated segments in p-DAME-co-HDFD even in low concentrations. [33] Furthermore, the observed threshold of 50 % of HDFD plasma-concentration, from which p-AA-co-HDFD becomes more hydrophobic, could be assigned to a higher extreme surface fluorine concentration after reorientation of perfluorocarbon chains during aging.

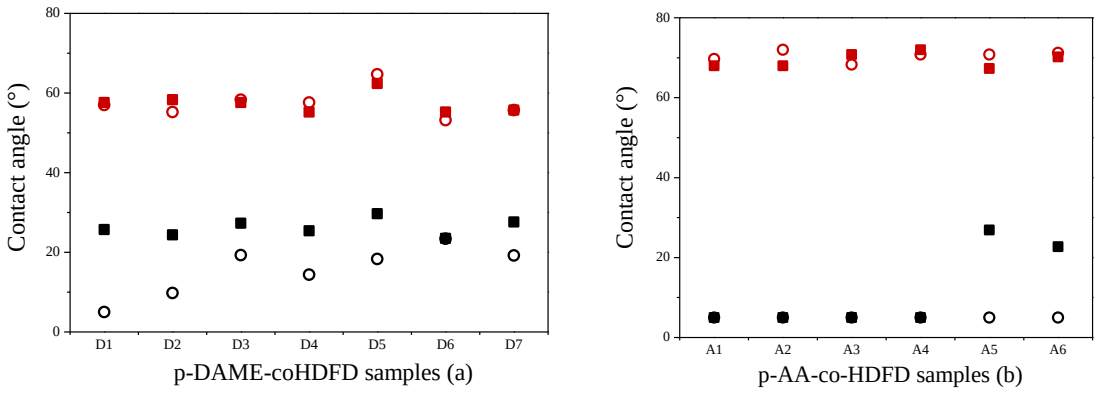

Figure 2. Water (black) and hexadecane (red) contact angles of fresh (circle) and 5CF aged (square) of p-DAME-co-HDFD (a) and p-AA-co-HDFD (b) films (standard deviation of all samples CA values ≤ 1 °).

Concerning WS aging where the layers are immersed during 10 days in water at 60°C, all p-DAME-co-HDFD and p-AA-co-HDFD coatings become more hydrophobic since WCA

increases from less than 20° to 44.7° - 59.0°. Besides, hexadecane drops completely wet on almost all aged plasma polymer surfaces. Such behavior may be explained by either reorganization of hydrophilic / hydrophobic chains, exsudation of additives from the PC substrate or delamination of thin film in aqueous environment.

III.2. Anti-fogging properties of the aged polymeric layers

5CF-aged films are exposed to water vapor in order to determine their anti-fogging properties (Table 2). Although all these aged p-DAME-co-HDFD and p-AA-co-HDFD layers meet anti-fogging standards, [34] i.e. WCA lower than 40° and HCA around 70°, only four aged coatings (A2, A3, A4, A6) remain transparent and a partial condensation is observed with A1, D6 and D7 samples. The same phenomenon is observed with a copolymer of hydroxyethyl methacrylate and perfluorosurfactants which was prone to fogging, even if its WCA < 10 ° and HCA around 60 - 70 °. [35] This illustrates the scale difference between a fog droplet, much smaller than that one recommended for the wettability measurement (around 1.7 mm of diameter) and, as a consequence, the fog droplet, as a liquid probe for wettability measurements is more sensitive than the conventional one and could be able to detect few hydrophobic chains while the other measure averages over a higher area.

As observed with contact angle measurements, the hydrophobic recovery phenomenon may be a reason which leads to the fog appearance. The WCA increase is less pronounced with p-AA-co-HDFD coatings than with p-DAME-co-HDFD ones. After thermal aging, and above the threshold HDFD plasma-concentration of 20 %, p-AA-co-HDFD is hydrophilic / oleophobic and anti-fogging (except A5) while no p-DAME-co-HDFD is transparent. In an opposite manner, the less efficiency of p-AA-co-HDFD (10 %) could be explained by a too low proportion of the oleophobic monomer.

Table 2. Influence of thermal 5CF-aging on the anti-fogging properties of p-DAME-co-HDFD and p-AA-co-HDFD coatings.

Sample	Anti–fogging test	Sample	Anti–fogging test
D1	Fogging	A1	Slightly fogging
D2	Fogging	A2	Anti-fogging
D3	Fogging	A3	Anti-fogging
D4	Fogging	A4	Anti-fogging
D5	Fogging	A5	Fogging
D6	Slightly fogging	A6	Anti-fogging
D7	Slightly fogging		

Concerning the WS aging, all aged samples of p-DAME-co-HDFD and p-AA-co-HDFD, whose WCA value is higher than 40°, show fog formation after being exposed to water vapor.

III.3. Evolution of surface chemistry of the polymeric layers after aging

XPS analyses are performed in order to investigate surface modification during the aging (Figure 3). F/C ratio tends to increase with increasing HDFD in the plasma mixture and it is more important in the case of p-AA-co-HDFD than p-DAME-co-HDFD. O/C ratio of p-DAME-co-HDFD seems not to be influenced by the HDFD amount and it is lower than that of p-AA-co-HDFD for which it decreases when HDFD proportion rises. F/C ratios of aged p-DAME-co-HDFD are found random around 0.21 - 0.42 and are lower than those of the fresh layers (except D1) whereas the O/C ratios are higher (0.21 - 0.23 against 0.17 - 0.21 for fresh layers). However, we have shown previously that WCA increases after 5CF treatment. These contradictory observations could be explained by the different depth of the two analyses. The contact angle measures the extreme surface while the XPS analyzes around 10 nm of thickness. Therefore, the motion of the fluorocarbon chains during aging does not change the total amount of fluorine analyzed by XPS but makes the extreme surface more hydrophobic. However, the decrease of F/C ratio for aged p-DAME-co-HDFD could be due to contamination that increases the C content. The increase of O/C ratio could be associated to post-oxidation during aging that

seems to be more important than contamination. [21,36,37] Concerning the acrylic acid-based co-deposits, no significant change of F / C and O / C ratios is observed between fresh and aged coatings which are from 0.33 to 0.67 and from 0.24 to 0.43, respectively. These observations indicate that the aging effect is less marked for p-AA-co-HDFD than p-DAME-co-HDFD; in other words, p-AA-co-HDFD resists to hydrocarbon contamination more efficiently than p-DAME-co-HDFD.

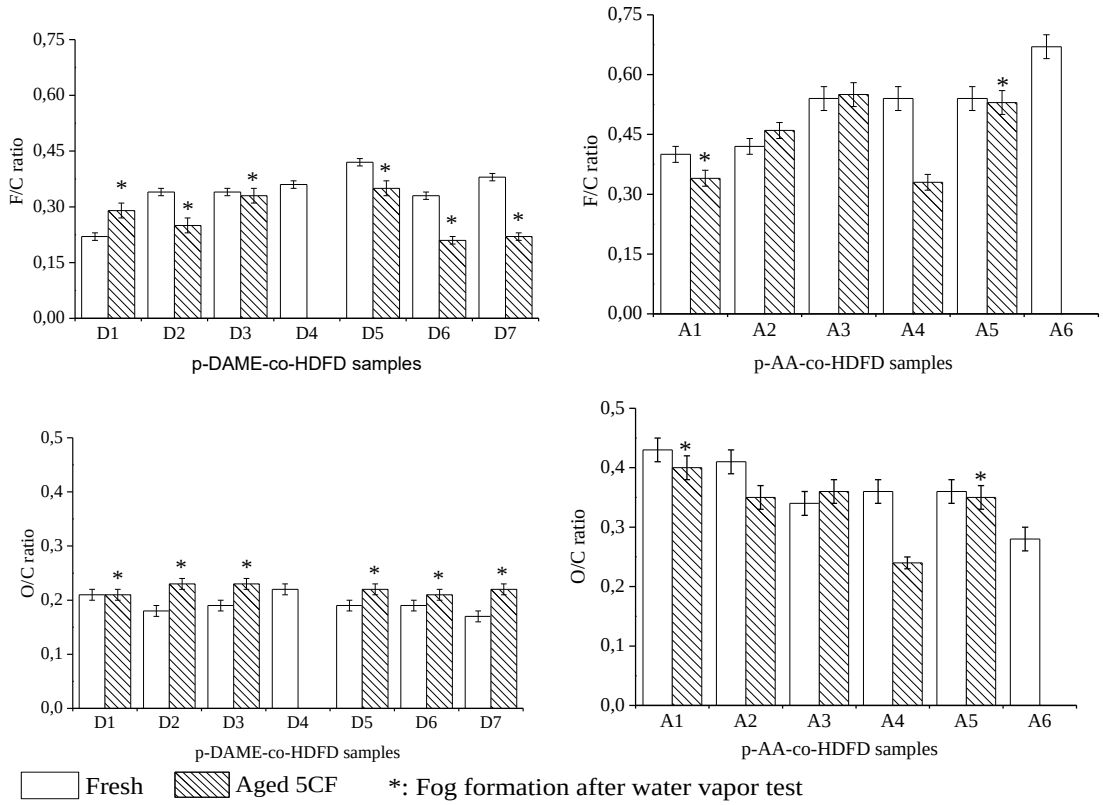

Figure 3. F/C (top) and O/C (bottom) ratios for p-DAME-co-HDFD (left) and p-AA-co-HDFD (right) fresh and thermal aged

To uncover the underlying mechanisms governing the chemical composition alteration of p-DAME-co-HDFD and p-AA-co-HDFD coatings before and after thermal aging, their C 1s high resolution XPS spectra are decomposed. These high resolution C1s peaks exhibit seven bands as shown in Figure 4 with their assignment. Only C1s XPS spectra of fresh and 5CF aged A5 and D5 are shown here (Figure 4). As an oleophobic layer is expected to resist to

contamination in order to keep its hydrophilicity, we suggest to study the long-term anti-fogging property by (i) the sum of CF_2 and CF_3 C1s XPS components (CF_2 + CF_3) to evaluate the amount of fluorocarbon groups and (ii) the ratio of CF_2 / CF_3 to estimate the length of fluorocarbon chains for p-DAME-co-HDFD and p-AA-co-HDFD coatings (Figure 5).

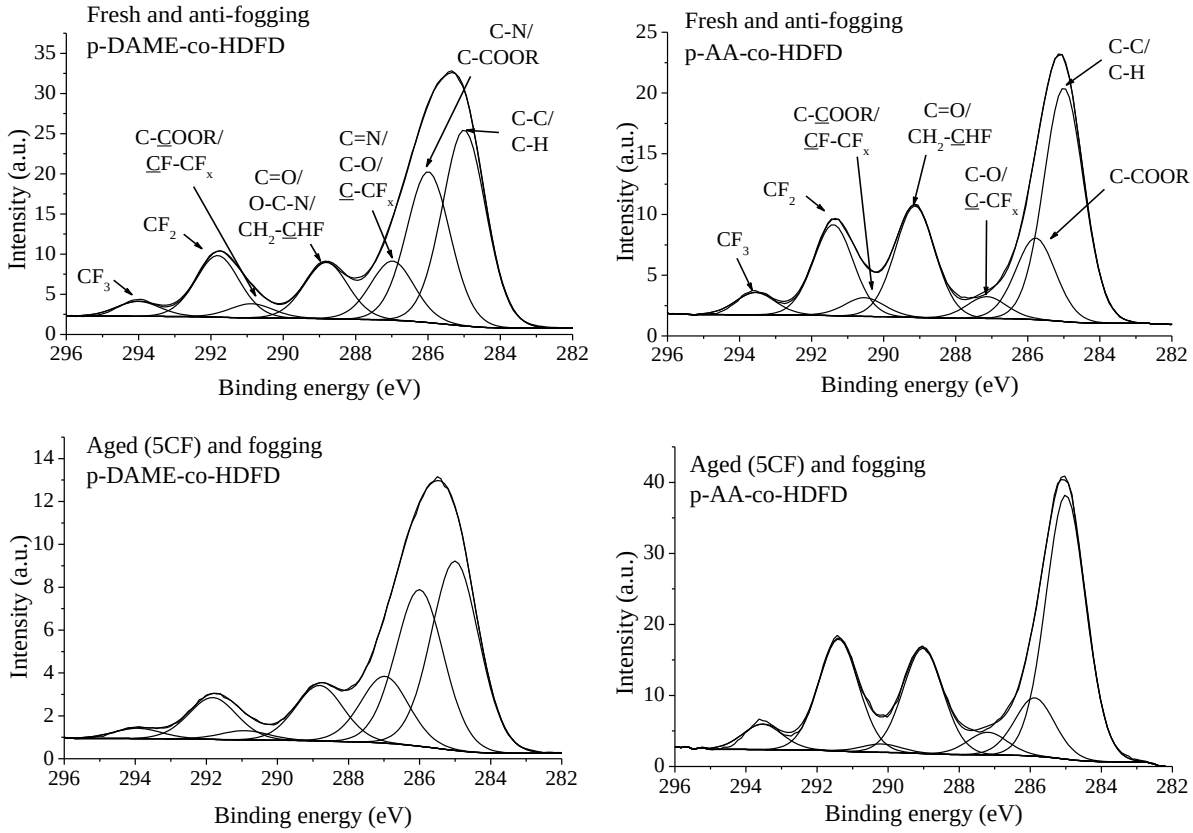

Figure 4. C1s high resolution XPS spectra of D5 and A5 before and after thermal aging

For each HDFD plasma-proportion, the sum of CF_2 and CF_3 of p-DAME-co-HDFD coating is lower than that of p-AA-co-HDFD when the fluorocarbon chains of the two types of co-deposits have about the same length (CF_2 / CF_3 comprised between 4 and 5). This could mean that the density of fluorocarbon chains in p-AA-co-HDFD is higher than that in p-DAME-co-HDFD. A higher [CF_2 + CF_3] amount in A2, A3, A4 and A6 samples (15.2 %, 23.3 %, 22.3 % and 30.2 % in fresh coatings respectively) than in A1 (13.7 % in fresh coating) and p-DAME-

co-HDFD coatings (4.7 % - 13.9 % in fresh coating) improves long-term anti-fogging property of plasma coating, as expected. But 5CF aged A5 forms fog after the water vapor contact whereas the fresh coating contains a high [CF_2 + CF_3] amount (22.5 %). It implies that high density of fluorocarbon groups is not the only factor which improve long-term anti-fogging properties. Moreover, A2, A3, A4 and A6 coatings keep their anti-fogging properties after thermal aging although their fluorocarbon chains length is in the range of the other p-AA-co-HDFD coatings (3.2 to 5.0), close to that of p-DAME-co-HDFD (3.7 to 4.7). Therefore, the long-term anti-fogging improvement of p-AA-co-HDFD compared to p-DAME-co-HDFD is not due to fluorocarbon chains length.

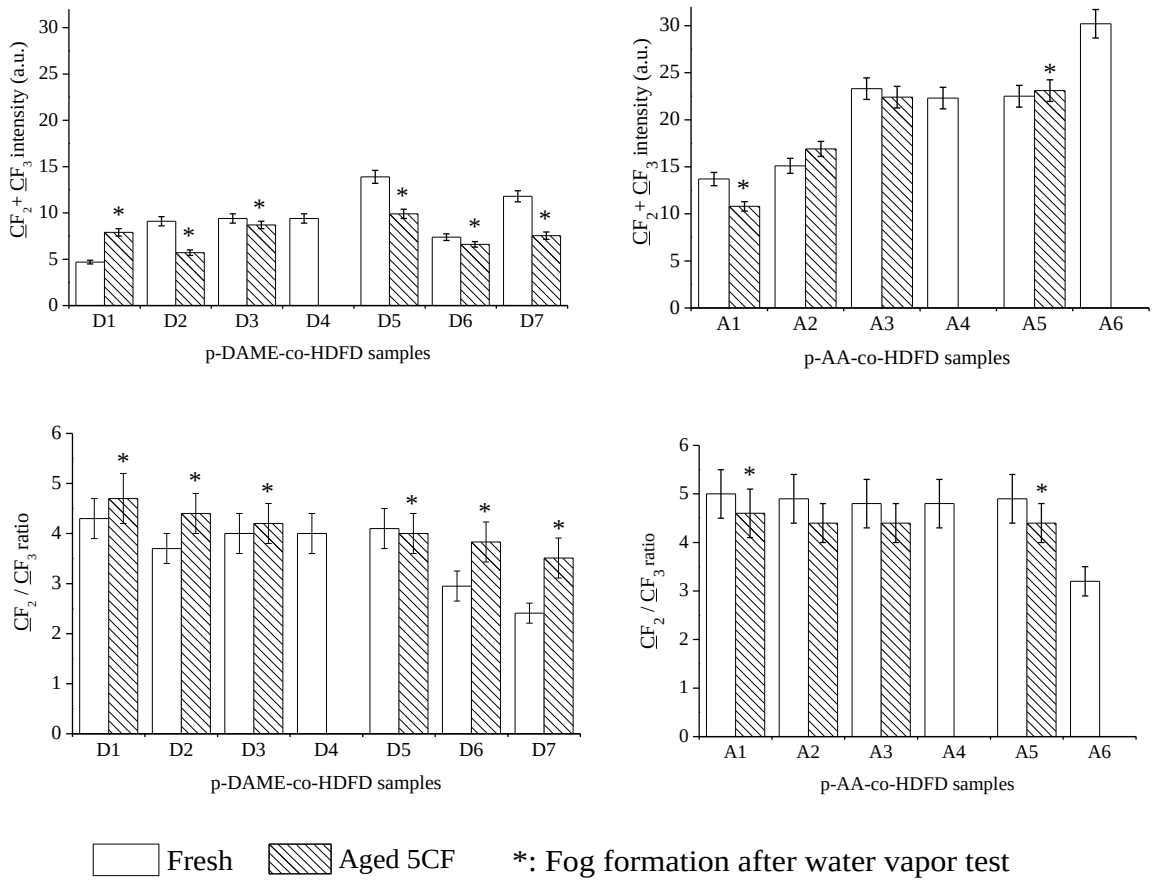

Figure 5. (CF_2 + CF_3) sum and CF_2 / CF_3 ratio (both calculated from C1s XPS peak) of p-DAME-co-HDFD (left) and p-AA-co-HDFD (right) fresh and thermal aged.

In conclusion, no significant change in the chemical composition after 5CF aging is observed by XPS analyses. Moreover, all plasma co-deposited layers are still hydrophilic / oleophobic as shown by contact angle measurements but only A2, A3, A4 and A6 aged surface retain their anti-fogging properties. From there, we may conclude that an anti-fogging surface is defined not only by the two wettability criteria: low WCA (≤ 40°) and HCA ≈ 70° but its transmittance has also to be preserved after water vapor contact. Even if the different observed behaviors of wettability and surface chemistry for these aged layers are related to the different analyzed thicknesses (first monolayer with contact angle and 10 - 20 nm with XPS), these analyses support the idea that chain motion may play a major role in the aging resistance as observed for anti-fogging property explained by the so-called "flip flop mechanism". [38] Indeed, the hydrophilicity decrease and the loss of anti-fogging property of all p-DAME-co-HDFD coatings may be due to slight flexibility of hydrophilic segments as with AA chains. [31,32] In order to give evidence of the influence of the polymeric chains motion on anti-fogging properties, p-AA-co-HDFD codeposits ([HDFD] = 20 %, t = 10 min) were prepared in such conditions that crosslinking should take place during the plasma-deposition. Within such a goal, some plasma parameters were increased as the discharge power from 10 W to 30 W, or the plasma pulse from 10 % up to 50 %, even more an argon plasma post-treatment was also applied. After the co-deposition and 5CF treatment, these layers are not anymore anti-fogging. Therefore, it may assume that quenched radicals formed during plasma co-deposition may react under aging process and may constrain chain motion required for keeping anti-fogging property. Furthermore, little hydrophilic chains must be flexible in order to form a durable layer. Finally, long-term anti-fogging behavior of p-AA-co-HDFD (20 % - 50 % HDFD) is mostly dependent on important flexibility of hydrophilic chains rather than its surface chemical composition.

The two types of co-deposited layers were dipped in hot water for 10 days and then analyzed by contact angle measures and XPS analyses. As all the aged p-DAME-co-HDFD (*[HDFD]* = 10 – 50 %, *P* = 10 W, *f* = 6 kHz, *d.c.* = 10 %, *t* = 10 - 30 min) and p-AA-co-HDFD (*[HDFD]* = 10 - 50 %, *P* = 10 - 30 W, *f* = 6 kHz, *d.c.* = 10 - 50 %, *t* = 10 - 30 min) coatings show about the same wettability properties, we only present XPS data of WS-aged D2 and A2. Wide XPS spectra of p-DAME-co-HDFD (20 %) after 10 days of immersion in water show a low fluorine proportion (0.4 %). Carbon concentrations increase from 62.6 % to 81.9 % and from 54.6 % to 79.5 % for WS aged amino-acrylate-based or acrylic acid-based plasma films while the oxygen percentages go from 11.5 % to 17.7 % and from 22.6 % to 19.4 %, respectively. These XPS data are close to those obtained for pristine polycarbonate showing 81.6 % of C and 18.4 % of O. It means that delamination of films from PC substrate occurs after wet surrounding aging, even if SEM pictures of aged samples (not shown here) did not confirm this.

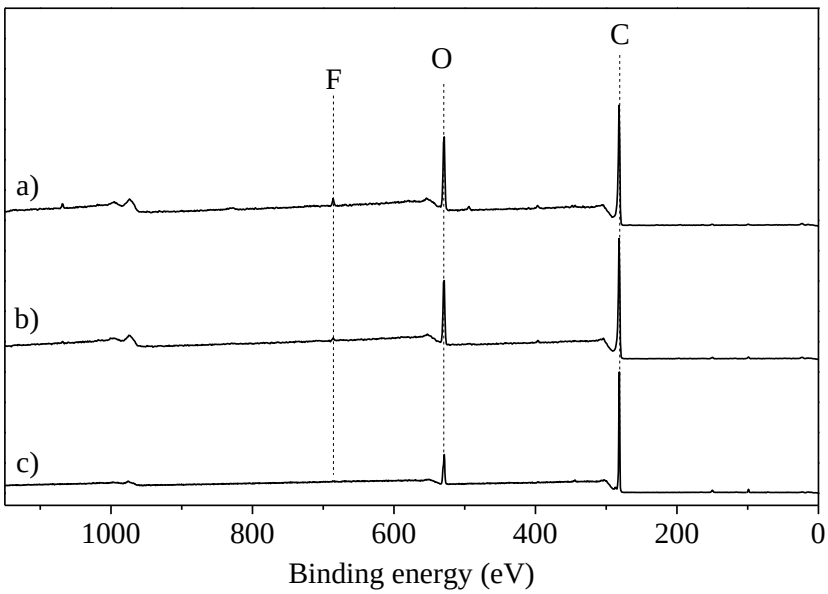

Figure 6. XPS survey spectra of a) D2 and b) A2 WS aged and coated on PC; c) pristine PC.

IV. Conclusion

Long-term anti-fogging properties of coatings plasma-synthesized from DAME / HDFD or AA / HDFD precursors were examined for two types of aging; the first one corresponds to a thermal effect while the second is focused on aqueous immersion.

Although the copolymer surfaces are still hydrophilic / oleophobic after the thermal aging with low WCA (< 30°) and HCA ~ 60° - 70°, only few p-AA-co-HDFD retain their good anti-fogging performances. Such a behavior is interpreted as a consequence of higher flexibility of hydrophilic segments in p-AA-co-HDFD compared to p-DAME-co-HDFD. This promotes hydrophilic / hydrophobic rearrangement in air - polymer interface allowing the formation of an uniform water layer after vapor water contact. We also demonstrated that with a HDFD plasma-concentration of 10 %, p-AA-co-HDFD does not retain its anti-fogging properties after aging. Post-oxidation and airborne contamination which lead to fog formation on all aged p-DAME-co-HDFD are detected by XPS analyses through the decrease of F/C and the increase of O/C ratios after 5CF treatment. Thermal stability of p-AA-co-HDFD with 20 - 40 % of HDFD in plasma phase was proved to not be influenced by fluorocarbon chains length but by the density of fluorocarbon groups even if it is not the only factor that can improve long-term anti-fogging properties.

After 10 days of immersion in water, all coatings lose their hydrophilic character by an increase of WCA to 47° - 59° and therefore their optical properties are altered with the fog formation. The contact angle and XPS results indicate that plasma coatings delaminate from the substrate.

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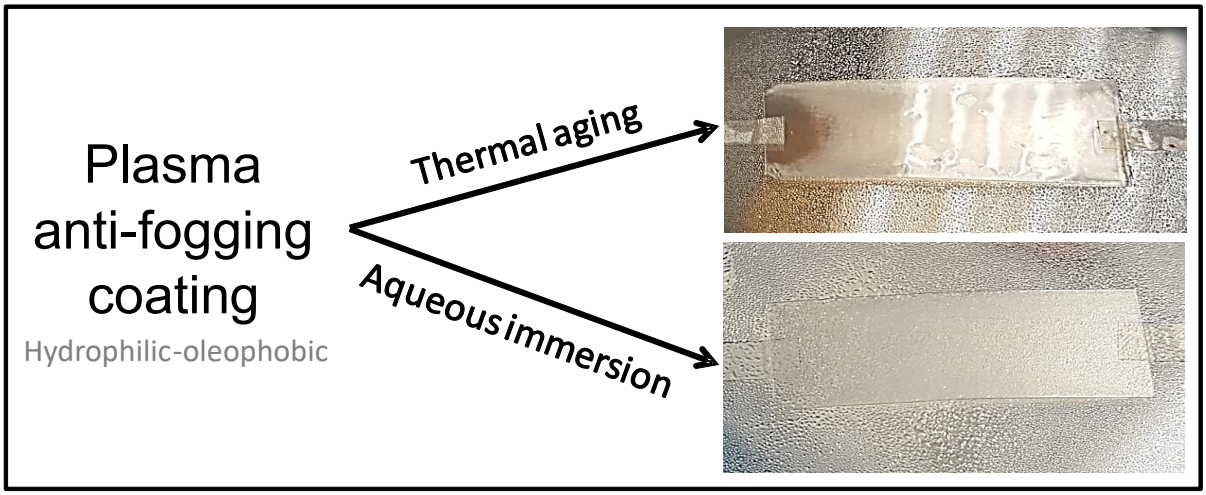
Highlights

- Fresh plasmadeposited (p-DAME-co-HDFD, p-AA-co-HDFD) are hydrophilic / oleophobic.
- Their long-term anti-fogging capability is studied in two different aging media.
- p-AA-co-HDFD (20 - 40 % HDFD) retain anti-fogging properties after thermal aging.
- p-AA-co-HDFD is more efficient in reducing the airborne hydrocarbon contamination.

Graphical abstract