Plasma copolymerization of antagonist monomers, a process towards original surface properties

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Abstract: Hydrophilic and oleophobic coatings were deposited onto polycarbonate (PC) thanks pulsed RF plasma of two coprecursors : 2-(dimethylamino)ethyl methacrylate / 1H,1H,2H-perfluoro-1-decene (DAME / HDFD) and acrylic acid / 1H,1H,2H-perfluoro-1-decene (AA / HDFD). The plasma parameter study indicated that AA / HDFD plasma deposition is more flexible in order to reduce airborne hydrocarbon contamination and therefore to improve the long-term antifogging performance.

Keywords: Plasma, copolymerization, anti-fogging.

1. Introduction

Anti-fogging coatings, mostly investigated in optics domains [1-3] are characterized with low water contact angle (WCA) < 40 ° in order to enhance the growth of a transparent and uniform water monolayer onto the substrate rather than the droplets formation affected the optical property. Such surfaces have been prepared from hydrophilic monomers bearing hydroxyl, carboxyl, amino or sulfonic groups [4-9] ; they could be also obtained from nanostructured coatings of oxide films such as silicium and titanium oxides [10-12]. However, such a hydrophilic layer with high surface energy could age because of the airbone hydrocarbons contamination and finally lose its antifogging property.

In order to prevent any ageing, the oleophobicity has been implemented thanks the addition of long perfluorocarbon chains that present a hexadecane contact angle around 70°, and therefore maintain unfavorable interaction with non-polar fluids [13,14]. Concomitant hydrophilic and oleophobic layers characterized with specific values of contact angles: water contact angle (WCA) < 40 °, hexadecane contact angle (HCA) ≈ 70 ° were proposed. Such a concept was applied for the antifogging plasma-layers prepared from the hydrophilic / fluorocarbon monomers mixture. Therefore, the DAME / HDFD and AA / HFDF plasma copolymerization was studied and the final properties were investigated by FTIR and XPS analyses, wettability. Finally, anti-fogging property and its long-term stabilility after storage in two conditions were determined.

2. Experiment set-up

Plasma was excited with a radio-frequency (RF-power 13.56 MHz) capacitive coupling plasma reactor (MG300S, Plassys) consisting in a cylindrical aluminum chamber (28 cm in diameter and 6.15 L volume) with two parallel circular electrodes (20 cm in diameter and are separated by 9.5 cm). The substrates were positioned on the cathode (lower electrode) during the film formation process. In order to ensure good adhesion of the deposit, the polymer substrate surface was pre-activated by plasma Ar (flow: F Ar = 10 sccm, discharge power P = 100 W, duration t = 30 s). Then, the precursor (DAME, AA, HDFD) were simultaneously but independently injected at the top of the chamber thanks to an electrode-integrated shower. Plasma conditions were maintained at P = 10W, d.c. = 10%, f = 6000 Hz, t = 10 min, p = 0.02 Torr during the copolymerization process.

Coated PC was aged by two processes: one with thermal effect (5CF) and the other with humidity effect (WS). In 5CF ageing, the sample was exposed to 5 cycles of [(16 h at 85 °C and 95 % humidity) – (3 h at -20 °C) – (6 h at 85 °C)]. In WS ageing, the films were immersed in water at 60°C during 10 days.

3. Results and discussion

The plasma copolymerization of the antagonist comonomers DAME / HDFD and AA / HFDF was studied in function of the partial pressure of the different precursors and consequently the fluorine proportion in the gas mixture.

Indeed, the colayer thickness is decreasing with the increase of HDFD proportion and is more pronounced in case of AA (Fig. 1). Such effect is explained by the relative dissociation energy of each chemical bond, the catalytic and degradative effect of fluorinated group [15,16] and also the poisoning effect of oxygen-contaning groups [17] more important with AA bearing a higher oxygen concentration compared to DAME ([O] = 44.4 % and 20. 4 % respectively).

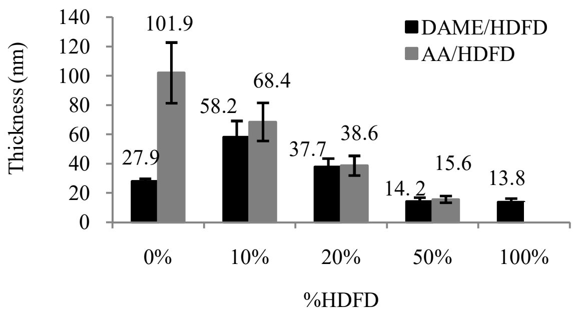

Fig. 1. Dependence of the thickness of DAME/HDFD and of AA/HDFD copolymers on HDFD proportion (*P* = 10W, *f* = 6 kHz, *d.c.* = 10%, *t* = 10 min).

Compared with the respective homopolymer FTIR spectra, the copolymer FTIR signature showed a combination of the different functional groups of the two homopolymers and the υCF_3 vibration band is increasing with the HDFD proportion. Moreover, the XPS spectroscopy (Table 1) reveals fluorine incorporation up to 10 % and 8.3 %, in case of AA / HDFD and DAME / HDFD copolymer, respectively for enriched plasma phase of 10-50 % HDFD. Furthermore, the high resolution C_{1s} spectra showed that increasing the HDFD concentration in the gas mixture leads to CF_3 and CF_2 rise but in a smaller proportion in the DAME / HDFD copolymer. CF_2 is the prevalent fluorinated group of AA / HDFD copolymer (12.5 % against 2.6 %) meaning that such a copolymer is bearing quite long perfluorinated chains.

Table 1 : Fluorine concentration and $(CF_2+CF_3)/(C\text{-}COOR/C\text{-}N)$ groups ratio (r) from XPS high resolution of C_{1s} of plasma-copolymer as a function of different HDFD % (*P* = 10W, *f* = 6 kHz, *d.c.* = 10%, *t* = 10 min)

HDFD %	10		20		50	
	F %	r	F %	r	F %	r
DAME/HDFD	14.4	0.2	21.4	0.2	25.1	0.5
AA/HDFD	22.0	0.8	22.8	1.4	28.3	1.6

HDFD homopolymer has a hydrophobic / oleophobic character with WCA = 107.0 ± 1.7 ° and HCA = 70.0 ± 0.6 ° while the water drop is immediately spread on the superhydrophilic DAME and AA homopolymers. All copolymer coatings with HDFD concentration lower 50 % show a simultaneously oleophobic / hydrophilic surface with WCA lower than 20 ° and HCA varying around 58.3 ° - 70.0 °. HCA of AA / HDFD (69.7 ° - 72.0 °) is higher than that of DAME / HDFD (57.0 ° - 64.7 °), such a result could be explained by the presence of long CF_x chain in AA / HDFD copolymer as demonstrated by XPS spectroscopy. These colayers are concomitant hydrophilic / oleophobic coating allowing the water spreading due to their hydrophilicity and reducing the hydrocarbon contamination due to their oleophobicity.

Therefore, their long-term antifogging performance was tested with two experimental procedures, one focused on thermal effect while the other emphasizes the atmosphere and its relative humidity. All acrylate-fluorinated copolymers and most of amino-fluorinated ones are not affected by the thermal ageing while any of them kept their anti-fogging properties after humid ageing. Such results could explained by the wettability alteration after the ageing. Indeed, after the thermal ageing, HCA of all samples did not significantly change, all surfaces are still oleophobic. But, after immersion in water at 60 ° during 10 days, the hydrophicity and the oleophobicity of all coating disappears. This suggests that such anti-fogging coatings were dissolved in the liquid water.

4. Conclusion

Hydrophilic / oleophobic copolymers were deposited on PC substrate from DAME / HDFD and AA / HDFD mixture thanks to the pulsed RF plasma. The influence of plasma parameters as the HDFD proportion in the gas mixture on the final chemical structure and the hydrophilic / oleophobic characteristics of the layer were studied for both hydrophilic monomers. Plasma phases containing 10 - 20 % HDFD induced the growth of coatings with anti-fogging property (low WCA around 20 ° and HCA value near 70 °). Such DAME/HDFD or AA / HDFD polymeric layers showed a long-term anti-fogging property when stored in dry atmosphere whatever the temperature.

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5. References

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