Surface nano-structuring of amphiphilic copolymer thin films via plasma polymerization

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Abstract: Plasma enhanced chemical vapor deposition (PECVD) has been previously used as a useful technique to prepare thin films of polymers. In the present work, we have applied (PECVD) technique for deposition and co-polymerization of 1H, 1H, 2H-perfluoro-1-decene (HDFD) and 2-(N,N-dimethylamino) ethyl methacrylate (DMAEMA) with various ratio of monomers by RF (13.56MHz) pulsed inductively coupled plasma. The resulted coatings were characterized by FTIR for chemical structure, profilometer for deposit thickness and AFM for morphology. The results show a chemical and morphological structure characterization.

Keywords: plasma copolymerization, HDFD, DMAEMA, structuration.

1. Introduction

Plasma copolymerization is becoming an attractive technique for the deposition of thin films by pulsed discharge of organic monomers vapors because of its possibility to prepare tailored films with pre-defined surface characteristics. The plasma copolymerization of carefully selected monomers may open new options to tailor a surface by combining properties of each of the monomers [1]. In the Past twenty years, many studies dealt with plasma copolymerization [2-7], and in past two years, the significant amount of work is focused on plasma copolymerization of monomers with physical-chemical antagonist proprieties (eg polar and non-polar), for the preparation of thin films functionalized which were structured to provide them with specific surface properties [3-7].

We studied the effect of discharge power, pressure, partial pressure of HDFD, deposition time and pulse time of radiofrequency (RF) pulsed plasma on the polymerization of HDFD and DMAEMA. The present paper focuses only on the influence of different ratios of HDFD in co-monomer mixture on the kinetics, chemical structure, and morphology of obtained thin films.

2. Experimental

Plasma deposition

The deposition experiments were carried out in a cylindrical aluminum capacitively coupled pulsed-plasma reactor which was pumped at 5.10^{-6} Torr. The reactor consisted of two parallel circular electrodes (diameter 30cm and thickness 1 cm) with 5 cm gap between them. The substrates (Si/SiO$_2$ wafer purchased from siltronix, KBr pellet from Sigma Aldrich and Mica from JBG-Metafix) were placed on the lower polarized-electrode. The reactor design is reported elsewhere [8]. Deposition time is limited to 30min in each case. The monomers 1H, 1H, 2H-perfluoro-1-decene (HDFD) were purchased from Sigma Aldrich, France and 2-(N,N-dimethylamino) ethyl methacrylate (DMAEMA) were purchased from Acros Organics, France. Copolymers of HDFD and DMAEMA were deposited on various substrates at a fixed plasma peak power (*P)* of 30W, duty cycle (*D.C.*) 50%, frequency (*f*) 30 kHz, for a total reactor pressure (*p*) of 0.02 Torr using a throttle valve. The reactor pressure was measured using a Pirani gauge (ACC 1009). Each monomer gas is injected from a glass tube container controlled by a valve (Nupro SS-4H) and the gas line is opened manually to introduce monomer in the discharge region of the chamber by an injection ring located above the substrate holder. The control of working pressure in the chamber handled by the butterfly valve coupled to Baratron gauge. After the pressure of the reactor went down to 5.10^{-6} Torr, the first monomer was injected to reach the desired pressure, then, the second monomer vapor was injected. When the total pressure set reach a stabilize value of 0.02 Torr, we turn on the pulsed plasma discharge by a radio-frequency (13.56 MHz) generator (Advanced Energy, Cesar 133) using a manual matching network. A summary of the experimental conditions used in the plasma copolymerization is given in Table 1.

HDFD (10^{-2} Torr)	DMAEMA (10^{-2} Torr)	$P_{HDFD} / (P_{HDFD}+P_{DMAEMA})$ (%)
0	2	0
0.56	1.44	28
1	1	50
1.3	0.7	65
2	0	100

Table 1. *Experimental compositions of the HDFD and DMAEMA plasma at 30W plasma peak power and 0.02 Torr.*

3. Results and discussion

*Chemical structure of plasma copolymer coatings*

FTIR spectra of layers of HDFD-DMAEMA (co)polymers synthesized by varying the amount of HDFD (28%, 50% and 65%) are shown in the figure 1 (left). When spectras of homopolymers pp HDFD and pp-DMAEMA are compared, one can notice that the spectra of these copolymers p-DMAEMA-co-HDFD (28%, 50% and 65%) retain different functional groups that exist in the structure of homopolymers. All spectras exhibit stretching vibrations of polymer backbone produced by ν as/sym C–H in the range 2950 to 27470 cm^{-1} associated with C=O stretching near 1750 cm^{-1} and C=C stretching near 1650 cm^{-1} , note that these bands are created from DMAEMA monomer. The bands between 1350 and 1140 cm^{-1} correspond to stretching vibrations of different bonds of CFx generated from HDFD precursor. However, the intensity of the bands characteristic of each homo-polymer increases or decreases depending on the composition of the starting monomer mixture, that is due to the ratio of one of the monomers relative to the other. This is confirmed in Figure 1 (Right), that shown the ratio of peak areas of CFx ($T_{1350-1140}$) on C=O and C=C bands (T_{1750} + T_{1675}) depending HDFD content in the mixture of co-monomer. This ratio increases with increasing proportion of the HDFD monomer.
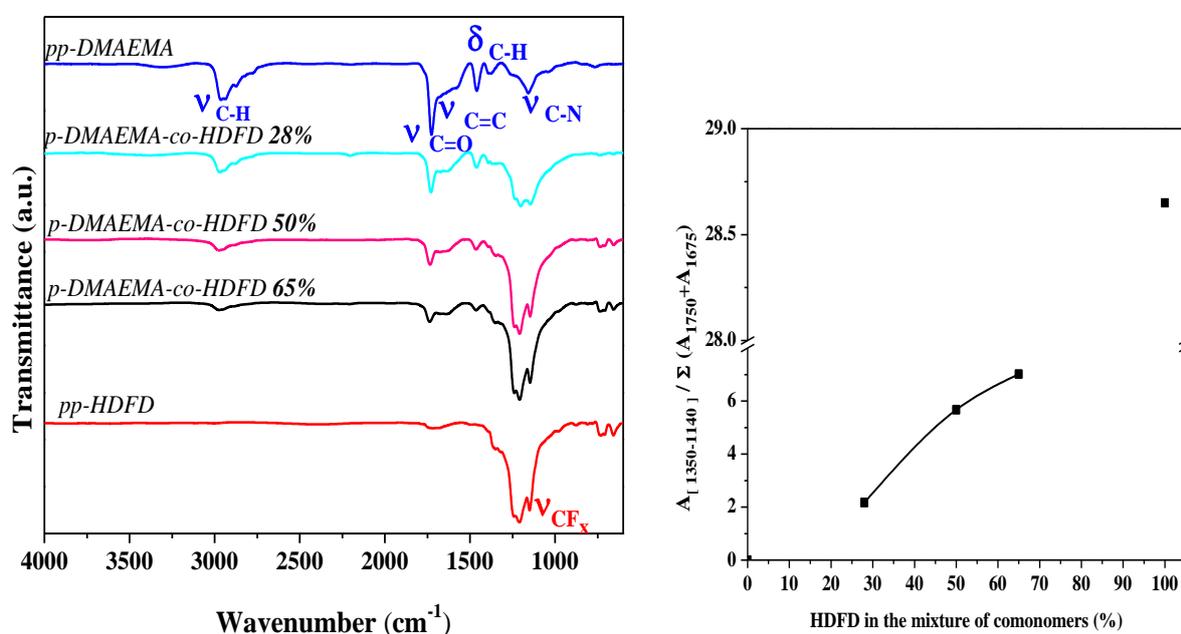
Figure 1. *FTIR-ATR spectra of HDFD and DMAEMA homo & copolymer coatings (Left). Evolution of ratio of peak areas of CFx ($T_{1350-1140}$) on the peak area of C=O (T_{1750}) and C=C (T_{1675}) by FTIR-ATR (Right).The layers are deposit at pulsed plasma effective power Peff = 15W.*

Kinetics of the copolymer deposition

Figure 2 (Left) present the evolution of the thicknesses of (co)polymers p-DMAEMA-co-HDFD deposited per pulse depending on the proportion of HDFD in the co-monomer mixture. We observe in our deposition conditions, a quasi-linear dependence of thickness per pulse with HDFD % in the mixture. The thickness per pulse increases with increasing content of HDFD in the composition of (co) polymers, this leads to increase in species responsible for polymerization. This observation suggests that HDFD is more reactive in the plasma phase, relative to DMAEMA due to the presence of fluorine which acts as a catalyst in the plasma phase. Kobayashi et al, [9] found that the addition of some halogenated compounds to hydrocarbon monomers greatly increases the polymerization rate. Thus, these compounds halogenated appear to act as a catalyst in gas phase for the plasma polymerization of hydrocarbons. Agostino has established a model AGM (Activated Growth Model) [10], show that ions play a role in the deposition by activating the surface of polymer (fluorine monomer = fluorocarbon). The rate of polymerization increases in the presence of charged particle; it's why pp-HDFD has a thickness per pulse more important than pp-DMAEMA. Also we can conclude from figure 2 (right) that the growth of layers controlled by fluorination process.
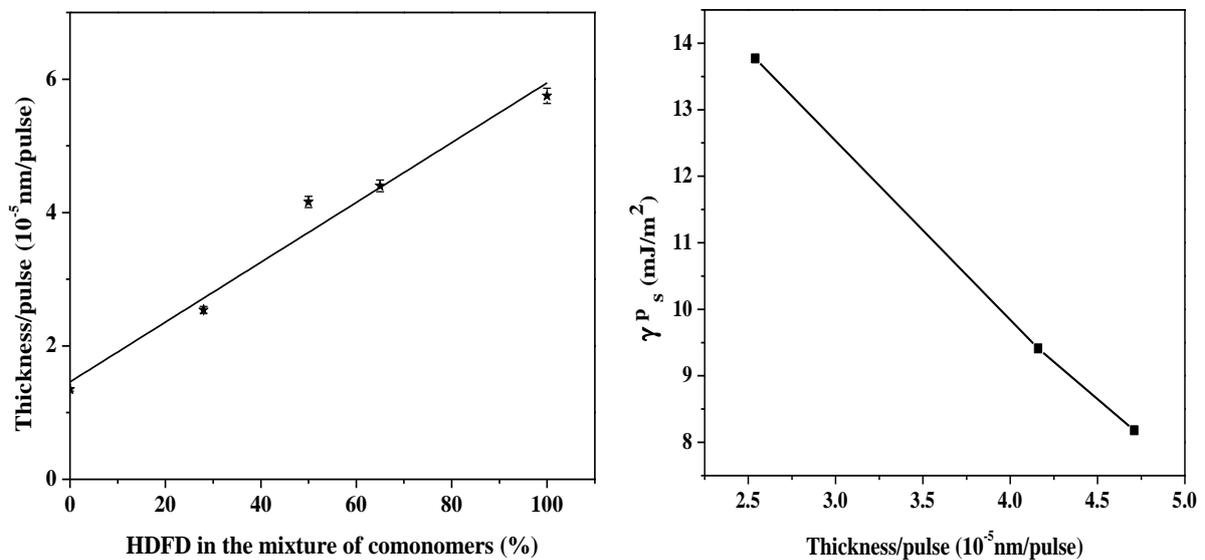

Figure 2. *Evolution of thicknesse per pulse at 30 W depending on the content of the copolymers p-DMAEMA-co- HDFD in HDFD (Left) and polar surface energy in function of thickness per pulse (Right).*

Morphologic of plasma copolymer coatings

Figure 3 show the morphology of various HDFD ratios in the copolymer layers p-DMAEMA-co-HDFD. The topography of films p-DMAEMA-co-HDFD (28%, 50% and 65%) for a power of 30W. the copolymer 28% of HDFD film appears plane and relatively

homogeneous, but the films of 50 and 65 % HDFD exhibit a structural variation and this is believed that this structural variation is rather due to aggregation than to degradation.

a **b** **c**
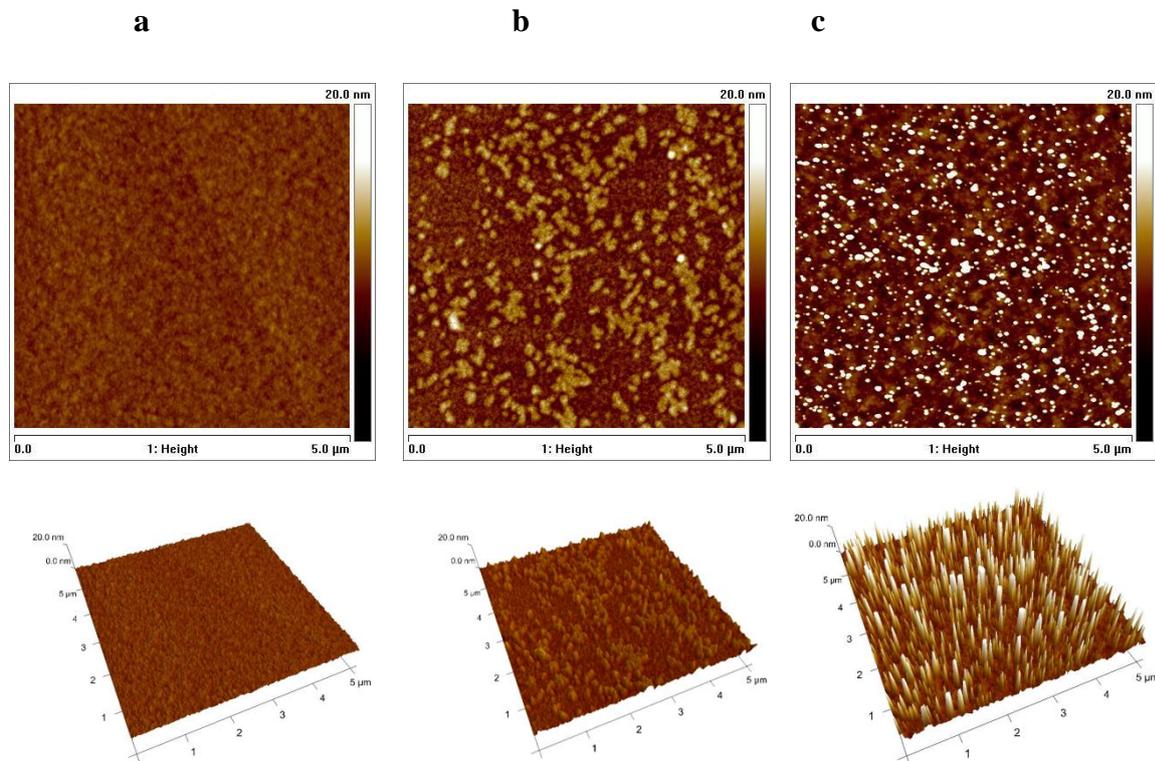
Figure 3. AFM picture topographic (top) and 3D image (bottom) of plasma copolymer layers obtained in pulsed modes (a) 28%, (b) 50 % and (c) 65% HDFD in the mixture of co-monomers. The layers are deposit at pulsed plasma effective power $P_{eff} = 15W$.

4. Conclusion

-Amphiphilic DMAEMA / HDFD copolymer coatings were successfully developed by single step plasma co-polymerization process, were DMAEMA is considered as polar and HDFD as apolar homo-polymers.

-FTIR-ATR (600-4000 cm^{-1}) spectral analysis of DMAEMA / HDFD copolymer coatings confirmed presence of different functional groups that exist in the structure of homo-polymers.

-Absence of interaction between precursors because no new bands d'absorption was created.

- This result tends to prove the presence of a chemical structuration of co-monomers mixture of copolymer; we can consider that we have obtained a mixture of polymers or bloc copolymers but not alternating or random copolymer.

- The growth of thin films copolymers was controlled by fluorination process.

- Morphology nano-structuring was obtained by plasma polymerization of amphiphilic copolymers.

5. References

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