

Low surface energy fluorocarbon coatings via plasma polymerization process: process optimization and protein repellent study

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Abstract: In the present study, low surface energy perfluorodecyl acrylate (PFDA) coatings and their copolymer coatings with diethylene glycol dimethyl ether (DEGDME) (i.e. PFDA-co-DEGDME) have been deposited through plasma enhanced chemical vapor deposition (PECVD) onto thermanox coverslips in a low pressure tubular inductively coupled RF plasma reactor. The influence of plasma parameters on surface chemical properties of the coatings were investigated by using fourier transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), x-ray photoelectron spectroscopy (XPS) and water contact angle (WCA). The protein repellent properties of the plasma polymer coatings have been investigated using quartz crystal microbalance (QCM).

Keywords: plasma enhanced chemical vapor deposition (PECVD), fluorocarbon coatings, protein repellent.

1. Introduction

Fluorocarbon coatings have numerous technological applications in various fields such as antifouling biomedical implants, microelectronics, integrated sensors, waterproofing and stain resistance textiles [1]. Fluorocarbons have always attracted significant attention for above cited applications due to their unique properties namely, inert, hydrophobic, oleophobic, high thermal stability, excellent chemical resistance, low coefficient of friction, weatherability, low refractive index and low dielectric constant [2]. Polymers with perfluoroalkyl chains are well known for their low surface energy and so high liquid repellency characteristics. Surface with regularly aligned closely packed CF_3 groups exhibited lowest surface energy of 6.7 mJ/m^2 well below the 18 mJ/m^2 value for poly(tetrafluoroethylene) [3]. Low surface energy coatings have been reported to be useful for preventing biofouling process due to their antifouling characteristics against biomolecules [4]. PECVD, an environmental benign process, has been widely used for deposition of functional polymer thin films for various industrial applications due to its inherent advantages [5]. The objective of the work is to optimize the plasma process for deposition of PFDA coating and investigation of protein repellent characteristics of PFDA and PFDA-co-DEGDME coatings.

2. Experimental

In the present work, low surface energy fluorocarbon coatings were deposited via plasma enhanced chemical vapour deposition of a high molecular weight fluorocarbon monomer, namely 1H,1H,2H,2H-perfluorodecyl acrylate (PFDA) and diethylene glycol dimethyl ether (DEGDME) from Aldrich, in the inductively coupled tubular radio-frequency (13.56 MHz) plasma reactor at a pressure of 0.5 mbar in continuous and pulse mode. The experimental setup is shown in figure 1. The effects of plasma

parameters on the chemical and morphological surface properties of the coating were investigated in order to optimize the plasma process. The properties of the coatings were investigated by using FTIR, FESEM, XPS and WCA. Plasma polymer coatings were evaluated for protein repellent properties using quartz crystal microbalance (QCM).

3. Results and discussions

3.1. PFDA coatings

The final applications of the plasma polymer coatings depend on its surface properties, namely chemistry and surface morphology. The coating chemistry controllability is highly desired for applications where surface chemical compositions play a vital role in dictating the device performance (e.g. biomaterials, sensors, catalysts, etc.). So it is important to achieve the molecular tailoring capability while retaining the enormous inherent advantages of plasma polymer coating technology. Therefore, we have investigated the effect of different plasma parameters on the chemistry as well as morphology of the plasma polymer coatings.

Figure 2 shows the FTIR spectra of PFDA coatings prepared under continuous wave (CW) and pulse plasma modes for two different average plasma power (P_{av}).

P_{av} = Duty cycle x peak power in pulse mode; and
Duty cycle (DC) = $T_{on}/(T_{on}+T_{off})$

It could be clearly seen that varying the plasma polymerization conditions change the local chemical environment in the plasma polymerized fluorocarbon PFDA coatings. The FTIR peak at 1741 cm^{-1} belongs to C=O stretching of acrylate group, whereas, the intense absorption band at 1205 and 1149 cm^{-1} are assigned to CF_2 asymmetric and symmetric stretching vibrations,

respectively [6]. There are two visible differences in the FTIR peaks prepared under pulse and CW mode: i) The intensity and sharpness of the IR peaks of CFX in PFDA coatings decreased drastically when the pulse plasma mode was switched to continuous mode retaining the same average power, and ii) The appearance of an additional intense peak at 1108 cm^{-1} indicated the formation of C-O-C groups on PFDA coatings in CW plasma conditions probably due to post-oxidation of the free radicals formed during the CW discharge (Figure 2).

These observations were further supported by XPS analysis (Table 1), which clearly indicated the lower concentrations of fluorine, CF_2 and CF_3 groups; and incorporation of oxygen in the form of COCF and O-C=O groups in case of CW plasma conditions as compared to pulse plasma conditions. So in pulse plasma condition, even though used at higher peak plasma power, offers the better chemical retention of the coating. Furthermore, there is an indication of change in the bonding environment of coatings prepared under different plasma conditions. In CW mode and at higher power conditions, the decrease in Fluorine and CF_2 , and increase in C-CF peak intensity in XPS indicates the crosslinking of polymer chains in the fluorocarbon coatings [5].

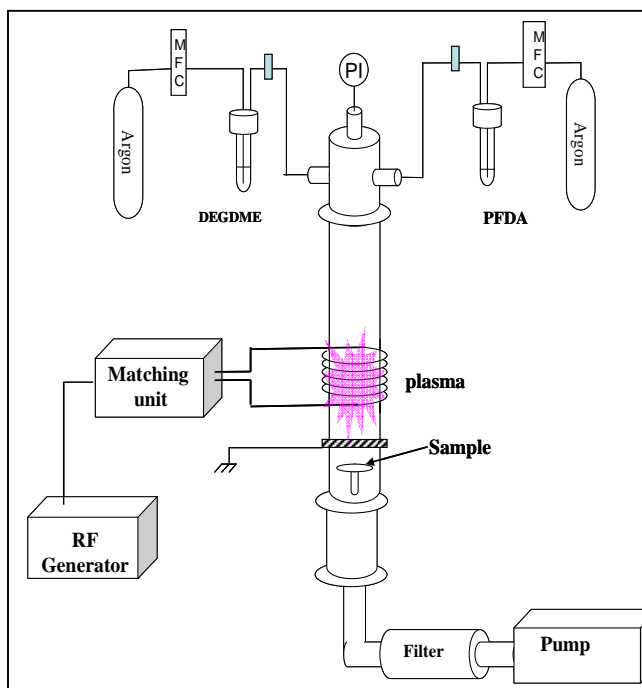


Figure 1: Experimental setup for PECVD of fluorocarbon coatings

Figure 3 depicts the FESEM images of PFDA coatings prepared under CW and pulse plasma mode (rest of

deposition parameters are identical). It indicates that PFDA coatings prepared in pulse plasma mode exhibited higher thickness of coating having rough and globular surface morphology with micro and nano-structures on the surface of the coatings and better hydrophobic characteristics (higher water contact angle) as compared to those prepared in continuous plasma mode (Figure 3). The lower thickness of PFDA coatings in CW mode is due to the predominance of etching over polymerization process.

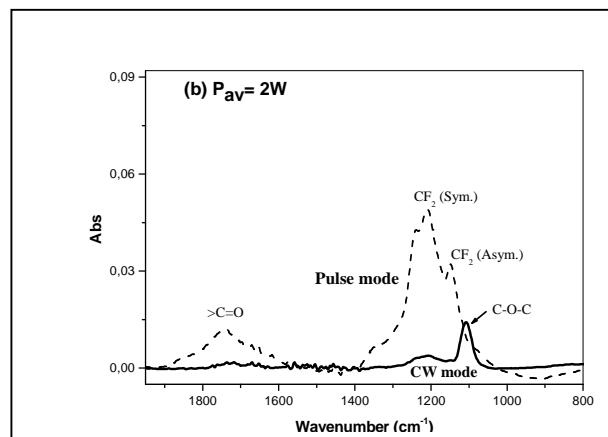
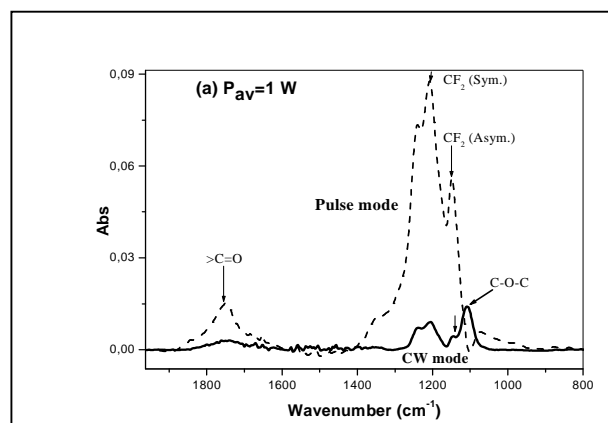


Figure 2: FTIR spectra of PFDA coating prepared under CW and pulsed plasma (DC= 25%) conditions. (a) $P_{av}= 1\text{ W}$, (b) $P_{av}= 2\text{ W}$ (treatment time =20 min).

The lower thickness of PFDA coating and dissociation of the fluorinated groups in CW mode justify the lower FTIR peak intensities in case of CW condition (Figure 2). Therefore, it is very important to note that PFDA plasma polymer films with two completely different chemical and morphological characteristics were obtained by simply changing the plasma conditions from pulse mode to the continuous wave mode, while keeping other experimental conditions constant.

The increase of the plasma power has a negative effect on the hydrophobicity and retention of CF_x group in PFDA coatings under both pulse as well as CW plasma conditions; however, the decrease in concentration of F, CF_2 and CF_3 in coatings is more prominent in CW as compared to pulse plasma process (Table 1).

Table 1. XPS analysis: coating compositions in at. % (CW Vs pulse at 10 Hz, 25% DC, 20 min)

Elements	CW- 1W	CW- 2W	Pulse- 4W ($P_{eq}=1W$)	Pulse- 8W ($P_{eq}=2W$)
F	48.1	44.0	50.3	48.8
CF_2	19.3	15.9	20.4	19.0
CF_3	3.4	3.5	4.0	3.7
COCF	5.3	8.1	4.8	5.9
CF:O-C=O	7.3	10.6	5.9	8.2

Surface energy of PFDA coatings were estimated by static contact angle measurement using two test liquids: water and diiodomethane using Owen and Wendt geometric mean equation [7]

$$(1 + \cos \theta) \gamma_l = 2[(\gamma_s^d \gamma_l^d)^{1/2} + (\gamma_s^p \gamma_l^p)^{1/2}] \quad (1)$$

and

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (2)$$

where θ is the contact angle, γ_s and γ_l are the surface free energies of the solid and liquid, respectively. The superscripts d and p refer to the dispersion and polar-force components, respectively.

In pulse plasma condition, duty cycle markedly influences the coating properties. The intensity of IR peaks for CF_x ($x=1-3$) of PFDA coating was found to decrease with the increase of plasma duty cycle, due to dissociation of CF_x groups in PFDA coating prepared at higher plasma duty cycle (data not shown). The surface energy of PFDA coatings increased with the increase in duty cycle of the plasma discharge (Figure 4). XPS study showed the ratio $CF_2/CF_3 < 7$ indicating the preferential orientation of CF_3 groups on the outer layers of the PFDA coating, giving rise to surface energy of as low as ~ 7.7 mJ/m² for PFDA coating.

PFDA-co-DEGDME coating

Recently, amphiphilic surfaces with surface heterogeneity have been targeted for biomedical applications including anti-biofouling surface [8,9]. In the present work, amphiphilic polymer coatings were deposited by plasma copolymerization of two polymer PFDA (hydrophobic) and DEGDME (hydrophilic) by PECVD process to study the synergic effect towards protein repellent properties of both polymers. Recently, it has also been proposed that the compositional and morphological nano-heterogeneity of amphiphilic polymer

coatings, generated due to the phase segregation of hydrophilic and hydrophobic domains, is the key to achieve antifouling surfaces [10].

FESEM was used to study the surface and bulk morphology of the coatings, which indicated that PFDA-co-DEGDME coating exhibit large and well ordered prominent nanostructures morphology versus less prominent globular surface morphology of PFDA coatings. PFDA-co-DEGDME coatings prepared in pulse plasma mode exhibited rough surface morphologies with nanostructures and better water repellent characteristics as compared to those prepared in continuous plasma mode. Furthermore, PFDA-co-DEGDME coating exhibited porous, worm-like bulk morphology, attributed to the phase-segregation of two incompatible polymer segments, unlike compact and homogeneous bulk morphology of pure PFDA coating (Figure 5).

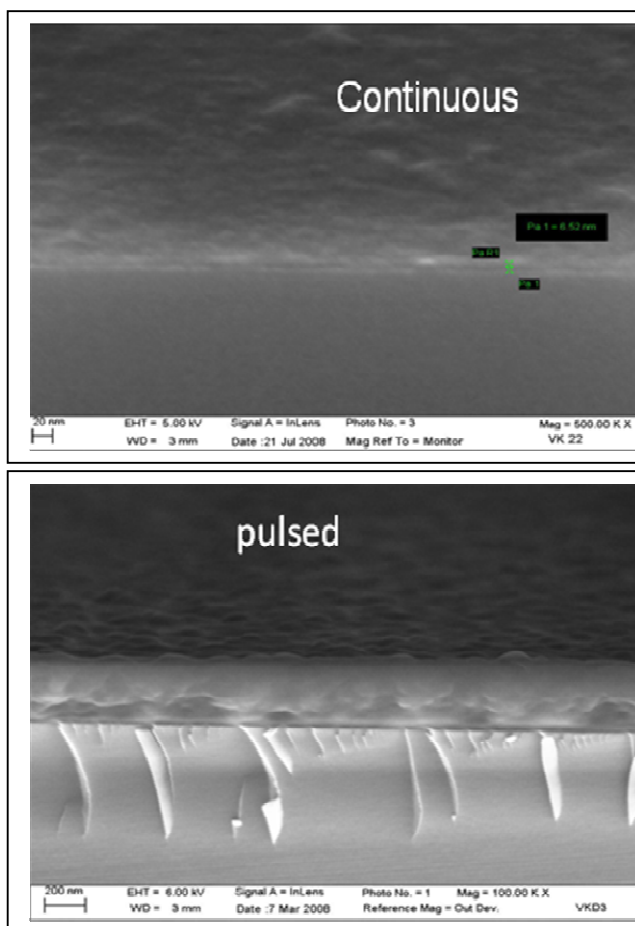


Figure 3: FESEM images of PFDA coating deposited under Continuous (thickness~10 nm) and Pulse mode (thickness~ 300 nm).

PFDA and PFDA-co-DEGDME coatings were tested for antifouling property against two different model test proteins namely; *Ovalbumin* and *human serum albumin (HAS)*, using quartz crystal microbalance (QCM). PFDA coatings were found to exhibit protein repellent property and decrease the adhesion of test proteins i.e. *Ovalbumin* and *HAS* by ~54 % and ~66 %, respectively, compared to uncoated gold QCM samples. Amphiphilic PFDA-co-DEGDME coating having surface nano-heterogeneity caused by phase segregation, and with optimized content of PEG like segments into PFDA coatings leads to ~100 % protein repellent property against the test proteins.

These results are in agreement with the results reported by Gan et.al, showing that incorporation of PEG like segments into fluorocarbon coatings decreased the protein biofouling [11]. These results showed that anti-biofouling property of inert fluorocarbon coatings can be further improved by copolymerization of fluorocarbon PFDA with DEGDME, leading to PFDA-co-DEGDME coatings having nano-heterogeneity due to phase segregation of two incompatible polymer components.

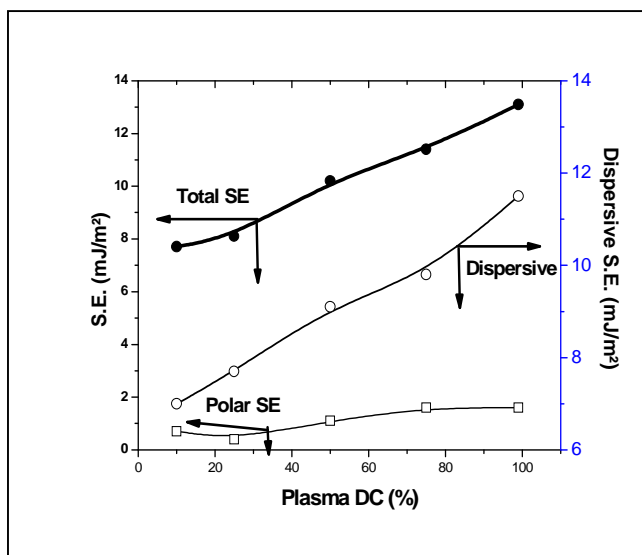


Figure 4: Effect of plasma duty cycle on the surface energy of PFDA coatings ($P_{pk}=1W$, $P=0.5$ mb)

Conclusions

The chemistry and morphological surface properties of the fluorocarbon coatings deposited via PECVD can be tuned by changing the plasma process parameters. Low surface energy PFDA coatings exhibit protein repellent property as compared to uncoated surface. PFDA-co-DEGDME copolymer coatings, obtained by plasma copolymerization of two incompatible polymers, showed further enhancement in protein repellent property, offering a new strategy to ward off biofouling problem.

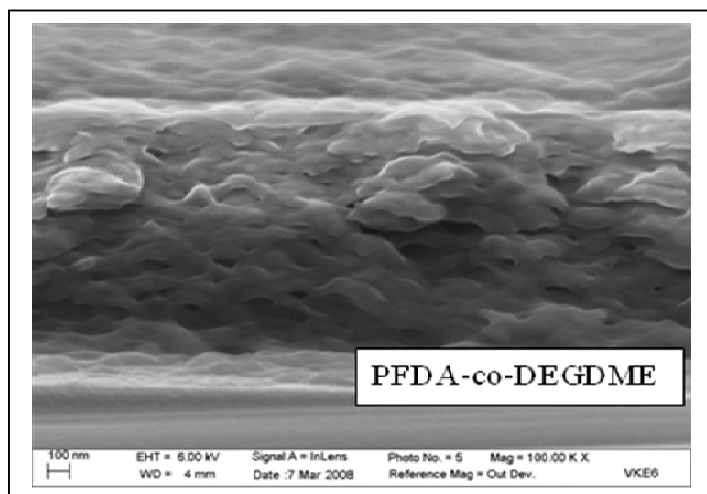


Figure 5: FESEM image of PFDA-co-DEGDME coatings (Pulsed plasma, 1W, DC= 25% P= 0.5mb)

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