Surface structuring and wettability control of Polyvinyl fluoride (PVF) using Extreme Ultraviolet (EUV) surface modification

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Abstract

In this study, surface modification of fluoropolymer Polyvinyl fluoride (PVF) films was performed using Extreme Ultraviolet (EUV) radiations to induce patterned structures on surface and to provide control over the surface wettability. Specially developed laser produced plasma based EUV source was used for surface structuring. The double stream gas-puff target was produced by injection of krypton and xenon (KrXe) gas mixture into a hollow stream of helium. Commercially available EKSPLA Nd:YAG 1.06 micron laser was used to irradiate the KrXe gas puff target with 3 nanosecond pulse duration having 0.8 J energy. The PVF films were irradiated with 50 and 200 EUV pulses. The surface characterisation of the pristine and EUV modified PVF polymer films was performed by Atomic Force Microscopy (AFM) for morphological modifications. To investigate chemical modifications, X-ray Photoelectron Spectroscopy was used. The wettability of the sample surfaces was examined by Water Contact Angle (WCA) measurements. EUV surface modification of PVF films resulted in formation of wall type rippled structures on the polymer surfaces. The surface roughness of the EUV treated surfaces was increased up to 287 nm and 21° reduction was observed in the WCA of the PVF films. Successful surface structuring and wettability control was obtained using EUV surface modification of PVF films.

Index Terms—**Extreme Ultraviolet, Surface Structuring, Wettability, Polymer Processing, Surface Modification, PVF.**

I. INTRODUCTION

The Polyvinyl fluoride (PVF) $-(CH_2CHF)_n-$ polymer exhibit high melting point, chemical inertness and high ultraviolet stability due to presence of fluorine atoms that form tight bond within hydrocarbon chains [1]. Due to excellent resistance of weathering, staining and chemical attack, the PVF is commercially well-known for coating applications in science and technology. The non-biodegradable capacity of PVF films encouraged to use them in biomedical engineering for longstanding performance. However due to low levels of biocompatibility, the PVF films could only be used with special coatings [2]–[4]. For example, the co-polymerization of PVF films with the grafting of N- vinylpyrrolidone demonstrated excellent resistance of bacterial adhesion of S. aureus, E. coli and P. aeruginosa [2]. It has been demonstrated that surface structuring of polymers resulted in improved biocompatibility. Moreover, the provision of wettability control of the PVF films is often desirable for various applications, such as making hydrophobic and hydrophilic surfaces, antibacterial surfaces, and enhancement of biocompatibility [5]. Nitrogen doping is often desirable to improve the performance of polymeric biomaterials used as implants. It has been demonstrated that nitrogen doping has resulted in improved hemocompatibility, fast healing around stent grafts, promotion of cell adhesion and proliferation, and provision of good control over biocompatibility by reducing allergic reactions [6]–[10].

In this study, the PVF samples were surface modified with Extreme Ultraviolet (EUV) radiations in the nitrogen environment. Laser plasma based EUV and soft X-ray sources have been demonstrated for various applications in science and technology [5], [11]–[14].

The nitrogen atoms were ionized by incoming ionizing EUV radiation and incorporated on to the surface of processed polymer sample. PVF polymer films were irradiated with increasing EUV pulses. EUV surface modification resulted in surface structuring and reduction in Water Contact Angle (WCA).

Following introductory section, this paper is organised as follows: the detailed experimental setup and materials used for the study are described in the materials and method section.

The results on modifications in surface morphology, chemical composition and wettability are presented and discussed, followed by the conclusion section.

II. MATERIALS AND METHODS

The PVF polymer films commercially available from Goodfellow Cambridge Limited, UK were used for this study. The polymer films were cut into 12 mm by 12 mm area and mounted on the sample stage of the EUV source. A laser produced plasma (LPP) based EUV source working at 10 Hz was used for the surface modification of the PVF films. A double stream gas puff target was created using electromagnetic valve system to inject KrXe gas mixture into the confining gas stream (Helium). He gas was served as confining gas to keep KrXe target dense for laser irradiation. A commercially available Nd:YAG laser (10 Hz, 1.06 μm wavelength, 3 nanosecond pulse duration, and 0.8 J energy) was used to irradiated gas target which resulted in formation of plasma releasing EUV photons. EUV radiations were collected using a glazing incidence gold platted ellipsoidal collector and delivered to sample processing chamber for PVF surface modification. An auxiliary gas inlet was used in the sample processing chamber to introduce nitrogen gas during EUV irradiation. An XYZ motorized stage was used for sample mounting to enable raster scanning of PVF films. The focal spot size of the incoming EUV photons was adjusted to get a 1.5 mm in diameter EUV trace on the sample. Therefore stage movements were controlled to achieve uniform 50 and 200 EUV pulses irradiation over 12 mm by 12 mm area of the PVF films. Further details about experimental setup have been reported in previous studies [15]–[18].

To investigate the influence of EUV surface modification of PVF films, pristine and EUV processed samples were characterized by different surface characterisation techniques. For surface structuring characterisation, commercially available Atomic Force Microscopy (AFM), provided by NT-MDT, Russia was used. The standard tip NSG03 (tip curvature 10 nm, spring constant 0.35-6.06 N/m, and resonance frequency 47-150 kHz) was used for measuring the pristine and EUV polymer samples. The AFM measurements were performed in semi-contact mode. For detailed investigations, the pristine and EUV treated samples were images at different scan areas [25 μm x 25 μm and 50 μm x 50 μm]. The acquired AFM images were processed using Image Analysis software provided by NT-MDT for quantitative investigation of the changes in the surface roughness of the polymer films.

For chemical modification investigations, sample surfaces were scanned with X-ray photoelectron spectroscopy (XPS) with analyzer R3000 from VG Scienta Sweden and X-ray lamp with from PREVAC sp. z o.o. CasaXPS software was used to perform the elemental characterisation of the obtained XPS spectra.

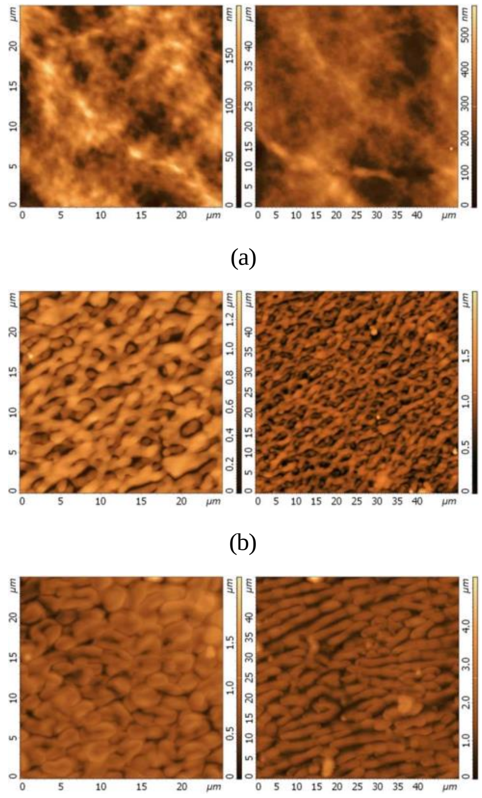
CAM 100 water contact angle measurement system supplied by KSV Instruments was used in static sessile drop mode to examine the modifications in the wettability of the polymer samples.

III. RESULTS AND DISCUSSION

The results obtained from AFM, XPS and WCA are summarized in Table 1.

A. Surface Structuring

The PVF foils were scanned by AFM before and after EUV surface modification for morphological characterization. Typically, the morphology of the laser ablation depends upon the nature of the material and their sensitivity to irradiating photons. Pin-point, delamination, fractures and cracking, and blistering are typical examples of laser induced damage. The pristine PVF foils were smooth without any visible structures (Figure 1a).



(a)

(b)

(c)

Figure 1 AFM images of PVF polymer samples scan at 25 x 25 μm^2 and 50 x 50 μm^2 area size (a) pristine sample, (b) PVF sample irradiated with 50 EUV shots, (c) PVF sample irradiated with 200 EUV shots

The average surface roughness (Sa) was about 40 nm. In case of PVF foils irradiated with EUV pulses for five seconds per mm of the sample (50 EUV pulses), the morphology of the foils was modified and wall type rippled structures were present on the polymer surface (Figure 1b). The average surface roughness was increased to 169 nm. The EUV surface modification for 20 seconds per mm of the sample (50 EUV pulses) strongly modified the PVF surface and pronounced wall type rippled structures appeared on the surface increasing the average surface roughness to 287 nm (figure 1c). The height of structures present on the PVF surfaces was in the range of about 80 nm to 1.3 μm. It has been demonstrated in the literature that the cells adhere and proliferate actively on the strongly roughed surfaces as compared to that of smooth or lower rough surfaces [19]. The wall-type rippled structures formed by the EUV surface modification could act as contact sites for cells to adhere themselves. Such adherence of cells commonly known as focal adhesion [8].

TABLE I. SUMMARIZED EUV SURFACE MODIFICATION RESULTS FOR SURFACE ROUGHNESS, WATER CONTACT ANGLE AND CHEMICAL MODIFICATIONS

EUV treatment	**Average Surface Roughness [nm]**	**WCA [degree]**	**Chemical changes [at. %]**			
			F	**O**	**N**	**C**
Pristine sample	40	85	35	0.7	0.0	64.3
50	169	74	11.9	8.6	2.6	67.9
200	287	64	3.6	6.6	13.4	76.4

B. Chemical Modifications

Pure and EUV treated PVF samples were characterized for chemical modifications using X-ray photoelectron spectroscopy (XPS). To detect carbon, nitrogen, oxygen and fluorine, the XPS scans were made for the detection of binding energies from 0 eV to 720 eV. Although the PVF samples were processed in vacuum conditions by keeping the pressure of sample processing chamber at $1x10^{-1}$ bar, oxygen atoms in the environment could be ionized and incorporate to the treated surface. This however could not be considered as impurity as oxygen incorporation was also demonstrated as good practice for biocompatibility control as oxygen containing functional groups mimic the structure of extracellular matrix (ECM) [20]. Additionally, oxygen treatment promotes protein adhesion and nerve cell adhesion [21]. The EUV photons take part in ionization of nitrogen atoms and laser ablation had wavelength of 10.8 nm corresponding to 112 eV energy.

Hence it is well understood that a single EUV photon has the capabilities to break several chemical bonds on the surface of the polymers as the EUV photon energy was well above the binding energies of organic polymer chemical bonds between carbon and carbon, carbon and nitrogen, carbon and oxygen etc. [5], [22]. The XPS spectra of pure and EUV irradiated PVF samples are presented in Figure 2 and the quantitative results of atomic percentage of elements were summarized in Table 1. The carbonization and defluorination was increased with increasing number of irradiated EUV pulses. The percentage of incorporated nitrogen atoms was 2.6% and 13.4% in PVF samples irradiated with 50 and 200 EUV pulses respectively. The amount of nitrogen doped by EUV surface modification (13.4% by 20 seconds treatment) was comparable to previous studies. For example, using nitrogen plasma, nitrogen atoms were incorporated 14% in PVF films by 600 second treatment time [23].

C. Wettability

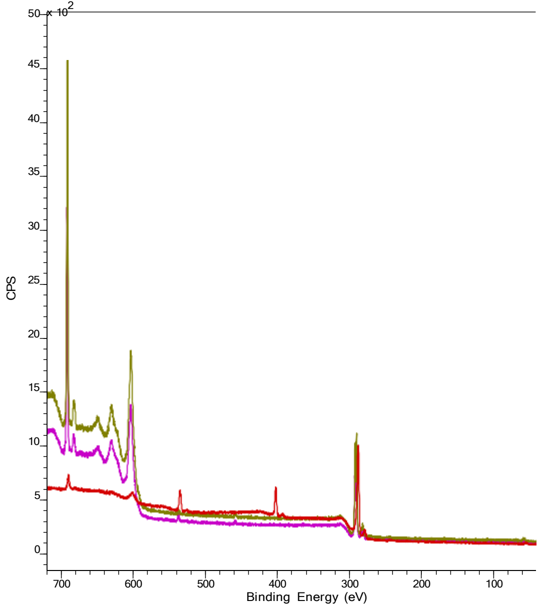


Figure 2 XPS spectra for pure and EUV irradiated PVF samples

The water contact angle (WCA) measurements of the pristine and EUV irradiated polymer surfaces were acquired. The WCA for pure PVF sample was found to be 84° (±1). The PVF films became hydrophilic by EUV surface modification. The WCA reduced to 74° (±2) and 64° (±2) for PVF foils irradiated with EUV photons for 5 seconds and 20 seconds respectively. The change in WCA occurred due to change in surface morphology and chemical composition or reorientation of molecules on the material surface. If the change in average surface roughness was less than 1 micron, the effect on WCA is negligible [31]. Therefore the incorporation of nitrogen atoms, carbonization and defluorination could possibly be the reasons for change in wettability of the PVF foils. The wettability measurement provides insight to biomaterial and biological world interface processes. It has been demonstrated that a moderately tuned hydrophilic surface promotes fibroblasts cell adhesion and proliferation [8], [5], [25].

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IV. CONCLUSION

In this study, surface modification of PVF films using EUV photons has been successfully demonstrated. The EUV surface processing of the PVF films induced pronounced wall type and rippled structures on the polymer surface. The incorporation of nitrogen atoms onto the surfaces of PVF films was successfully obtained. The roughness of the polymer films surfaces was increased by increasing the number of EUV pulses irradiation. PVF films became more hydrophilic as the WCA of the processed films was decreased up to 64°. The laser plasma EUV source based on gas puff target was successfully demonstrated for surface structuring and wettability control of PVF films.

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