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Formation of different microstructures on a polyethersulfone film following XeCl laser irradiation

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Abstract
Laser irradiation parameters, especially the laser fluence and the number of pulses are very important factors affecting microstructures formation and improvement of the surface characteristics in different medical, electronic and the other industrial applications. Information about the fluence domain and the number of pulses for the formation of the structures is very important and determines the desirable or unwanted effects of the laser irradiation on the surfaces regarding the desired applications. In this paper Polyethersulfone films were irradiated with a XeCl laser at fluences above the ablation threshold. The effects of the laser fluence and the number of pulses on the formation of different microstructures on the surface were investigated.

Keywords: polyethersulfone, XeCl laser, microstructure, Cone- periodic ripples

1. Introduction

Studies on laser ablation of polymers have been started in the early 1980s [1, 2]. Creation of a new surface with properties specially designed for a desired technique is as an important trend in laser ablation [3-6]. In this scope, development of effective ablation or laser machining techniques for making micro-optical components has been the key factor in the birth of new photonic devices and systems [7]. Excimer laser ablation of polymers can produce a variety of morphological features on the surface. Formation of these microstructures depends on the experimental conditions such as the laser wavelength, the laser fluence, the number of pulses and the material parameters such as the absorption coefficient at the laser wavelength [8]. Material removal from the surface following laser ablation is one of the most important reasons for the formation of these microstructures. The onset of material removal occurs at defined laser threshold fluence [8, 9]. The microstructures may form on the surface below or above this ablation threshold through the surface modification and (or) ablation. Creation of microscopic structures on the surface may be useful for improving adhesive bonding, surface friction and fabricating filtration, catalytic, field emission cathode and light-trap devices [10].

Polyethersulfone (PES) is a thermoplastic polymer used for a variety of applications ranging from microfluidics to biological ones especially for ultrafiltration membranes [11]. Despite its popularity as a membrane material, the hydrophobic nature of Polyethersulfone is disadvantageous in blood contact work. The hydrophobic character of polysulfones surface that is a reason for platelet adhesion and biofilm formation on medical implants is a consequence of their chemical structures [12]. A number of efforts have been made with the aim of modifying polysulfons surface using different methods such as gamma radiation [13], UV radiation [14], plasma treatment [15, 16], and chemical reaction of hydrophilic components on the membrane surface or bulk PSf [17].

Laser irradiation is known as a standard method for physical and chemical modification of different material in medical application [18, 19]. Chemical surface modification during laser ablation depends strongly on the laser fluence. Laser irradiation can affect hydrophilicity of a surface by changing the surface morphology, surface chemistry, surface roughness and surface charges. In our last papers [20-26], we presented the effect of KrF, XeCl and ArF laser irradiation on the surface chemical, morphological, wettability, bio and blood compatibility of the polyethersulfone surface

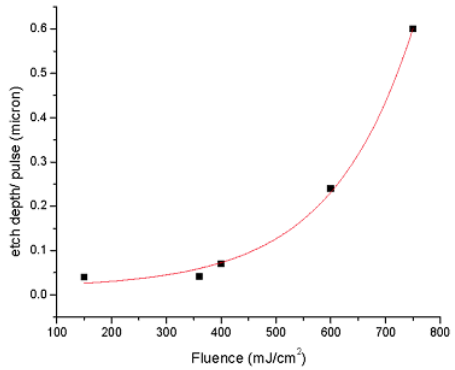

Figure 1. The etch depth per pulse plotted as a function of the fluence.

based on the UV laser ablation mechanisms. We have shown that depending on the laser wavelength, irradiation dose and the fluence, the PES surface undergoes different chemical modifications, and various microstructures are formed on the surface. These modifications play an important role in the surface wettability, blood and biocompatibility. As a result information about the laser parameters (e.g. fluence domain and number of pulses) for the creation divergent of the structures is critical. The aim of this paper is to determine how microstructures change on the polyethersulfone films following a XeCl laser irradiation by the laser fluence and the number of pulses, above the ablation threshold.

2. Experiments

Polyethersulfone (PES, Ultrason E6020, M_W=58000, flakes) was supplied by BASF Co. PES was compressed at 250°C and 30 Mpa, using a laboratory press (Mini Pest press, 10 Poyosciti, Japan), into pieces of 80-100 μm in thickness and 30×10 mm in dimensions.

XeCl laser (Lambda physics, λ=308 nm, τ= 25 ns) was used as the laser source. The laser beam was focused on the sample with a cylindrical quartz lens with focal length of 35 cm. The incident fluence F was adjusted by varying the voltage of the laser source and the central, fairly homogeneous area of the beam was selected using a 2×10 mm^2 slit.

Scanning electron microscopy (SEM: Tescan Vega\\LMU) was applied for the observation of the microstructures on the surface after irradiation.

3. Results and discussion

3. 1. XeCl laser ablation mechanism for PES ablation

Excimer lasers are well known to be applied in micromachining of the polymeric material with submicrometer precision. The interaction of excimer laser with a substance typically results in the occurrence of photothermal processes that heat the sample and/or photochemical processes that cause the direct bonds to break in molecules constituting the substances. The formula that has been widely used to interpret the ablation data is given by:

$$l_{\text{photochemical}} = (\frac{1}{\beta}) \ln \frac{F}{F_T} \quad , \tag{1}$$

Where l is the etch depth (per pulse), β is the absorption coefficient, and F_T is the threshold fluence of ablation.

On the other hand in the thermal description of laser ablation, the etch depth versus fluence can be understood by the Arrhenius thermal model, given by

$$l_{\text{photothermal}} = A_1 \exp\left[-\frac{E_1}{RT}\right] \quad , \tag{2}$$

where T is the temperature, R is the gas constant, and A_1 and E_1 are the pre-exponential factor and activation energy, respectively.

The etch depth per pulse as a function of fluence for XeCl laser ablation of PES is shown in figure 1. The etch depth exponentially depends on the laser fluence and can be described using the Arrhenius function eq. (2). As it was mentioned, the laser wavelength is an important parameter in absorption of a polymer, and the mechanism for material removal. The value for the absorption coefficient of PES film at 308 nm is about 120 cm^{-1}. In a weakly absorbing polymer a number of incubation pulses are needed for ablation to occur for a given fluence. For the ablation of PES at 308 nm, the ablation begins after number of 58 and 35 pulses for fluences of 150 and 400 mJ/cm^2, respectively [26]. The etch depth then increases exponentially as a function of the fluence. These results show that at 308 nm, etching of PES occurs with thermal characteristics seen at visible and infrared wavelengths. A full description about the mechanisms of XeCl laser ablation of PES is given in ref [26].

3. 2. Formation of microstructure on PES film surface following XeCl laser ablation

Structures developed on surfaces following laser irradiation can be classified into coherent and non-coherent structures. Coherent structures are directly related to the coherence, the wavelength and the polarization of the laser light, while for non-coherent structures such direct dependence is not observed. Conical and ripple structures (non-coherent and coherent structures, respectively) are induced by laser irradiation of polymer surfaces. The structures induced by laser irradiation of polymer surfaces have been investigated by numerous research groups [22–25, 27-32] towards understanding of the mechanisms responsible for their formation. In several cases the structures may be an undesirable ‘defect’ on ablated surface, whereas in other cases they may be used for the modification of polymer surface properties.

In general the most common reasons for development of microstructures on the surface following laser irradiation comprises the following [22]:

(i) thermal process,
(ii) the nonlinear relation between the etching rate and the incident laser fluence,
(iii) different etching rate of amorphous and crystalline regions,

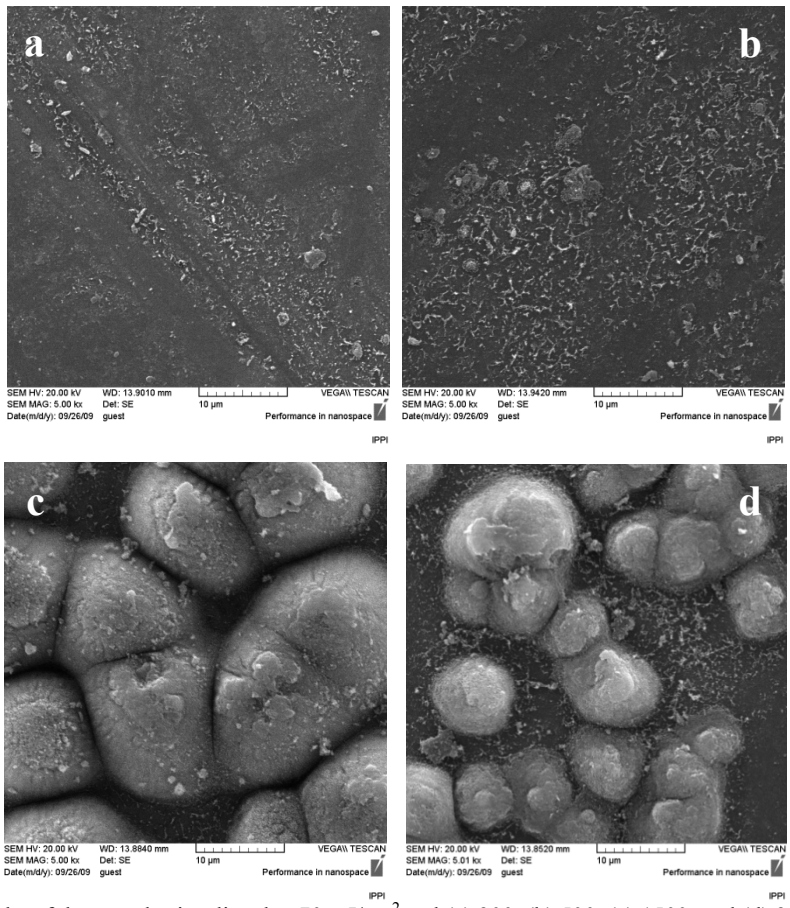

Figure 2. SEM micrographs of the samples irradiated at 70 mJ/cm^2 and (a) 300, (b) 500, (c) 1500, and (d) 3000 pulses

(iv) interference between incident and the scattered parts of the laser beam,
(v) devitrification of the film surface at temperatures above the characteristic T_g ,
(vi) the laser beam shielding by the re-deposited ablation debris and possible impurities,
(vii) relaxation of the frozen-in stresses [33].

Development of the structures depends on the laser parameters as well as the sample properties. The structures may develop following the laser irradiation below or above the ablation threshold. The threshold fluence of XeCl laser ablation of PES was experimentally found to be 60 mJ/cm^2. During XeCl laser ablation of PES above the ablation threshold, different microstructures (e.g. cones and ripples) appear on the surface depends on the laser fluence and the number of pulses. Figure 2 (a) to (d) shows typical SEM micrographs of PES films irradiated at a fluence of 70 mJ/cm^2, pulse repetition rate of 1 Hz and different number of pulses. It is observed that the material removal from the surface begins to start after about 300 pulses of laser irradiation (figure 2 (a)). As it was mentioned above, because of the weak absorption of the PES at 308 nm, ablation occurs first through incubation followed by subsequent ablation. During the incubation period, the material is converted either photochemically or thermally into a more highly absorbing material and the modified material then ablates as if it strongly absorbing at the laser wavelength [20, 26]. When the number of pulses is increased, the net material removal increases. Conical structures appear on the surface with 1500 pulses. The cones number is increased by increasing the number of pulses while it is decreased by increasing the laser fluence. The fluence range for the cone formation is found experimentally to be about 70-150 mJ/cm^2.

Formation of conical structures has been explained mostly by laser beam shielding either from local enrichments and material impurities on the surface or from photo-fragments and debris condensed on the surface between laser pulses. We have investigated the cone formation following XeCl laser ablation of PES film at different laser beam spot sizes [20]. The irradiation with different spot sizes of the laser beam at a given fluence and number of pulses leads to changes in the shape, the size and the density of the cones. Although the number density of the cones increases with the decrease in laser spot size, the size of them decreases and a more dense structure forms on the surface at larger spot size. The ablated plume of debris ejected from the large spot size has a larger area of high density, while the debris ejected from the smaller spot size consists of low ablated mass. Considering the axial expansion and radial velocity of the ablated debris as well as the collision

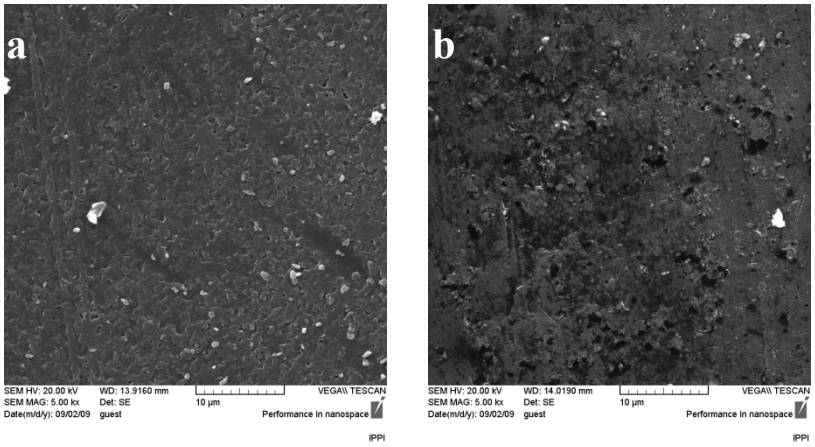

Figure 3. SEM micrographs of the samples irradiated at 150 mJ/cm^2 and (a) 5, and (b) 30 pulses

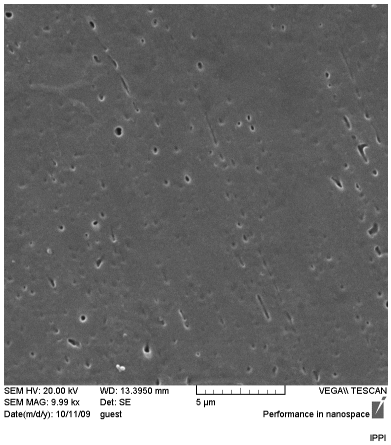

Figure 4. SEM micrograph of the sample irradiated with 5 pulses of 300 mJ/cm^2.

between them we have shown that cones form mainly because of the ablated debris deposits on the surface during the laser ablation [20].

At higher laser fluence of 150 mJ/cm^2, sponge like structures are formed on the surface with 5 pulses (figure 3 (a)). By increasing the number of pulses the structures disappear and no define pattern is observed on the surface (figure 3 (b)). With more increase in the laser fluence, i.e. at the fluence of 300 mJ/cm^2 and with 5 pulses, some micro-holes are formed on the surface (figure 4). The number of holes increases by increasing the number of pulses. The reasons for the formation of the holes are not completely understood. The holes may represent voids formed under the action of a tensile wave developed in the lower layer of the surface upon irradiation [34].

Periodic and perpendicular ripples are formed on the surface with 1500 pulses at a fluence of 400 mJ/cm^2 (figure 5). The ripples are vertical in the center of the ablated area (figure 5 (a)) and horizontal in the edge (figure 5 (b)). The period of the ripples is ~ 1µm in both cases. Ripples oriented at random are formed on the surface at the fluence of 750 mJ/cm^2, and with 30 pulses (figure 6).

Ripples are coherent microstructures observed on the surface of a wide variety of materials after irradiation with excimer lasers. Ripples origin in most cases is supposed to be interference of the incident and reflected/ refracted laser light with the scattered light near the interface since their period depends on the wavelength and polarization of the laser light and the angle of incidence [32] and orientation of the ripples determined by the polarization of the laser beam. It has shown that the orientation of the ripples formed following XeCl laser ablation of PES depends on the irradiation angle and the polarization [35]. However, here we observe that the orientation of the ripples is also changed with laser fluences. On the other hand, the ripples formed here do not seem to be the same as coherent ripples resulting from the interference of the incident and the scattered beams, since their period ~ 1µm is not in the order of the laser beam wavelength. Moreover the orientation of the ripples also is different in the edge and the center of the ablated area. Formation of these ripples may be understood by considering the thermal properties of PES. The XeCl laser beam can deeply penetrate into the films under the ablated area because the XeCl laser line corresponds to the absorption edge of the polymer films. Then the local temperature on the surface of the irradiated area would be rapidly raised and a pool of fluidized material would be formed [35], leading to

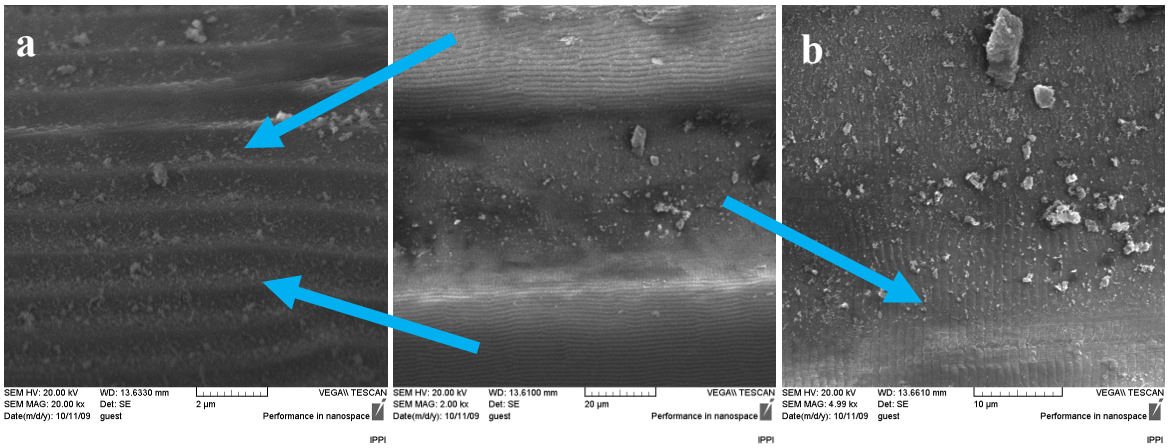

Figure 5. SEM micrographs of films irradiated with 1500 pulses at the fluences of 400 mJ/cm^2 (middle one). The arrows show a magnified image of the selected parts: (a) the edges part and (b) the center part of the picture.

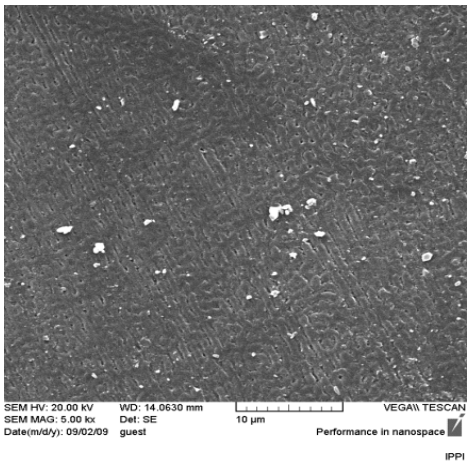

Figure 6. SEM micrograph film irradiated with 30 pulses at fluences of 750 mJ/cm^2.

structure formation with the interactions between the successive pulses and the fluid. The stress released following laser irradiation [33, 36] or devitrification of the film surface at temperatures above the characteristic glass transition temperature (T_g) of the polymer [22, 36] may also lead to the micro ripple formation on PES surface. However, a full investigation of the reasons for formation of these structures especially the ripples would be the subject of another paper.

4. Conclusions

Following XeCl laser ablation of polyethersulfone, conical, ripple and sponge-like structures were developed on the surface. The laser fluence and number of pulses for onset and development of the structures was determined. It was shown that the formation of the structures depends on the fluence and the number of pulses. Cone formation begins at laser fluences just above the ablation threshold and the adequate number of pulses; it goes on within a narrow range of fluences, and stops at higher fluences. At higher laser fluences sponge-like structures as well as periodic and random ripples are formed on the surface upon laser irradiation. The possible mechanisms for their formation were explained.

References

1. Y Kawamura, K Toyoda, and S Namba, *Appl. Phys. Lett.* **40** (1982) 374.
2. R Srinivasan and S Mayne-Banton, *Appl. Phys. Lett.* **41** (1982) 576.
3. A P Mello, M A Bari, and P J Prendergast, *J. Mater. Pro. Tech.* **24** (2002) 284.
4. D Krajnovich, *J. Appl. Phys.* **82** (1997) 427.
5. P Parvini, P B Jaleh, and B Sajad, *Lasers and Electro-Opt. Soci*., LEOS. The 14th Annual Meeting of the IEEE **2** (2001).
6. B Jaleh, P Parvin, M Katoozi, Z Zamani, and A. Zare, *Rad. Measure,* **40**, 2–6 (2005) 731.
7. Y T Chen, K Naessens, R Baets, Y Sh liao, and A A Tseng, *Optical Review* **12**, 6 (2005) 427.
8. T Lippert and J T Dickinson, *Chem. Rev.* **103** (2003) 453.
9. D Y Kim, K C Lee, C Lee, and J. Korean, *Phys. Soc.* **44**, 2 (2004) 341.
10. L L Sartinska *et al*., *Appl. Surf. Sci.* **253** (2007) 4295.
11. K Norrman, P Kingshott, B Kaeselev, and A G Siahkali, *Surf. Interface Anal.* **36** (2004) 1533.
12. Dattatray S Wavhal, Ellen R Fisher, Desalination **172** (2005) 189.
13. S Mok, D J Worsfold, A Founda, and T Matsuura, *J. Appl. Polym. Sci.* **51** (1994) 193.
14. J Pieracci, J V Crivello, and G Belfort, *J. Membrane Sci*. **202** (2002) 1.
15. K S Kim, K H Lee, K Cho, and C E Park, *J. Membrane Sci.* **199** (2002) 135.
16. M L Steen, L Hymas, E D Havey, N E Capps, D G Castner, and E R Fisher, *J. Membrane Sci.* **188** (2001) 97.

17. D Pospiech, K Eckstein, L Haussler, H Komber, D Jehnichen, and K Grundke, *Macromol. Chem. Phys*. **200** (1999) 1311.
18. A Haruyama, J Kato, A Kameyama, Y Hirai, and Y Oda, *Laser Phys*. **20** (2010) 881.
19. X Jiang, H M Ge, J J Liu, and Q S Ren, *Laser Phys.* **21** (2011) 548.
20. H Pazokian, S Jelvani, J Barzin, M Mollabashi, and S Abolhosseini, *Opt. Commun.* **284** (2011) 363.
21. H Pazokian *et al.*, *Laser Phys.* **22**, 5 (2012) 922.
22. H Pazokian *et al*., *Appl. Surf. Sci.* **258** (2011) 169.
23. H Pazokian *et al.*, *J. Micromech. Microeng.* **22** (2012) 035001.
24. H Pazokian, *et al*., *Appl Phys* A, DOI 10.1007/s00339-012-7142-9 (2012).
25. H Pazokian, S Jelvani, M Mollabashi, J Barzin, and G AzizabadiFarahani, *Appl. Surf. Sci.* **257** (2011) 6186.
26. H Pazokian, M Mollabashi, S Jelvani, J Barzin, and S Abolhoseini, *Optical Engineering* **50** (2011) 084301.
27. T Lippert, J T Dickinson, *Chem. Rev.* **103** (2003) 453.
28. H Niino and A Yabe, *J. Photochem. Photobiol.* A **65** (1992) 303.
29. R J van Gutfeld, F A McDonald, and R W Dreyfus, *Appl. Phys. Lett.* **49** (1986) 1059.
30. N Mansour and K J Ghaleh, *Appl. Phys.* A: *Mater. Sci. Process.* **74** (2002) 63.
31. J E Andrew, P E Dyer, D Forster, and P H Key, *Appl. Phys. Lett.* **43** (1983) 717.
32. D Bäuerle, "*Laser Processing and Chemistry*", Springer, Berlin (2000).
33. N Bityurin, E Arenholz, N Arnold, and D Bäuerle, *Phys, Rev.* E **75** (2007) 041603.
34. I A Paun, A Selimis, G Bounos, G Kecskemeti, and S Georgiou, *Appl. Surf. Sci.* **255** (2009) 9856.
35. A Yabe, and H Niino, *Mol. Cryst. Liq. Cryst.* 224, 1 (1993) 111.
36. E Rebollar *et al*., *Langmuir* **27** (2011) 5596.