XeCl laser treatment of polyethersulfone membrane in the air and water

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Abstract. XeCl laser irradiation of Polyethersulfone membranes in air and water were done. The irradiated surface were modified chemically or morphologically depends on the laser parameters and the mediums in which irradiation is done. The results in improving the surface hydrophilicity and biocompatibility for the biological applications were compared.

1. Introduction

When a biomaterial contacts tissue fluid or blood, its surface comes in to contact with the physiological environment. Since, many implantable biomaterials are constructed from polymeric materials, the biocompatibility of these materials is critical in their biological applications such as blood and cell contact works. The surface morphology and the surface chemistry specially wetting properties of the surface can significantly affect the extent of these interactions [1].

Nowadays laser irradiation is known as an appropriate method for both chemical and morphological modification of the materials used in different industries, especially medical demands [2-4]. Laser processing can perform in ambient air, vacuum or in the presence of a gas or liquid. Laser interaction in the presence of liquid mostly consists of conversion of part of the light energy into a mechanical impulse, which transports material and induces shock waves. Also in some cases dissociation products react chemically with materials. Most of these effects can be achieved using neutral liquids, but water is the most common, cheap and safe medium which used for wet etching.

Laser interaction in water has been studied since the 1970s and the commercial applications of water-assisted laser cutting, shock processing and surface cleaning from particulate contamination is now commercially available [5].

Polyethersulfone (PES) is among polymeric materials for medical applications. It is a derivative of high temperature engineered thermoplastic polysulfone polymer. It is frequently used for various medical applications such as membranes for hemodialysis and medical implants [5-7]. Unfortunately, the low hydrophilicity of Polysulfones has undesirable effects on its blood contact works [6, 8].

In this paper XeCl laser treatment of polyethersulfone membranes in air and water is investigated and the results of improving the surface hydrophilicity and biocompatibility for the biological applications are compared.
2. Materials and Methods

2.1. Materials preparation
Polyethersulfone (PES, Ultrason E6020, MW = 58,000, flakes) supplied by BASF Co. was employed as main polymer and polyvinylpyrrolidone (PVP, K90) provided by Fluka Co. was used as additive. Dimethylacetamide (DMAc) (Aldrich) was used as the solvent and pure water as nonsolvent. The phase inversion method [9] was used for the preparation of membranes. The polymer solutions of membranes containing 18% (wt) PES and 3% (wt) PVP in DMAc were used.

2.2. Laser irradiations
XeCl laser (Lambda Physics, 308 nm, \(\tau = 25\) ns) was used as irradiation source. The laser was operated at repetition rate of 1 Hz. The central part of the beam was selected by an aperture. The samples were irradiated at various fluences in two different environments (air and water).

2.3. Sample characterization
The morphology and hydrophilicity of the surface before and after irradiation was examined by scanning electron microscopy (TESCAN, Vega series) and statistic water drop contact angle measurements (contact angle goniometer (Krüss G10)), respectively. Attenuated total reflectance (ATR) spectra for determination of chemical changes on PES membrane surfaces were recorded using a FTIR spectrophotometer (Perkin Elmer, Model: Spectrum-100) in the region 650 to 4000 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\).

Cell culture study was done using L929 mouse cells for surface biocompatibility measurement.

3. Results and discussions

3.1. The morphology of membranes
Figure 1 shows the SEM images of the surface morphology and the cross section of the non-irradiated polyethersulfone membrane. As it can be seen in figure, the membrane consists of a very thin and dense skin layer overlaying on a thick and highly porous sub layer.

![Figure 1. SEM micrographs of (a) the surface morphology and (b) cross section of Polyethersulfone membrane](image)

3.1.1. Irradiation in the air. When PES membrane is irradiated in the air with 45 pulses at a fluence of 50 mJ/cm\(^2\) (Figure 2a), the skin morphology changed and a wavy pattern formed on the surface. This deformation of the skin could be a result of thermal interaction of the laser and the membrane skin. With increasing the laser fluence the skin is removed from the surface at local positions and it is
Ablated completely at a fluence of 85 mJ/cm² (Figure 2b). More increase in the laser fluence leads to removing the sub layers and observation of the inner structure of the membrane. Figure 2c shows sample irradiated at a fluence of 120 mJ/cm² and 45 pulses.

3.1.2. Irradiation in the water. The samples were putted in distillate water and the laser beam was focused through the water on to the target surface. The height of water above the membrane was about 3-4 mm. Since water has low absorption at 308 nm, the same fluences as above were applied for irradiation of the samples in water. This helps us to avoid the results may happen due to large difference in laser fluences.

Here the laser pulse interacts with both the water and the membrane which causes vaporisation of the solid target and a small amount of water. Irradiation at all fluences (50, 85 and 120 mJ/cm² (Figure 2, (d, e and f))) has no effect on the surface morphology.

3.2. Chemical modifications

High power laser interaction with the sample both in air and water produce plums of the particles due to the material ablation. In the initial process the interaction of light with the sample surface causes to vaporization of the surface material and a small amount of surrounding liquid. Then chemical reactions between the ablated species and molecules in the liquid can subsequently occur. The ablated plum of the particles expands more freely in air than water. This lead to formation of molecules contained atoms from the target material and the water.

Figure 3 shows FTIR spectra of PES membranes before and after irradiation at fluences of 50 and 120 mJ/cm² in air and water. A new peak at 1734 cm⁻¹ assigned to C-O bond, appeared following irradiation of the samples at a fluence of 50 and 120 mJ/cm² in air. The peak intensity increases with increasing the laser fluence and then decreases at higher laser fluences (not shown). Formation of this peak is due to interaction of the laser with the O₂ molecules of the air and the carbon atoms of the
membrane. There are also two bands located at 1665 cm\(^{-1}\) and 3430 cm\(^{-1}\) that are associated with the C=O vibration for PVP molecules and the OH stretching vibration of water molecules. The presence of OH group is related to the membranes preparation method which used a water bath to form a porous membrane. Since porous materials may hold in their pores small amounts of water that in practical terms, are almost impossible to remove, this peak is observed in the IR spectra. The intensity of this peak decreases during irradiation due to material removal from the surface and vaporization of free water.

The peak intensity is higher for samples irradiated with the similar conditions in the water. This probably is related to the confinement of the ablated products with water and then increasing the number of reactions with water molecules near the surface of membrane.

3.3. Contact angle measurements and surface hydrophilicity
Table 1 shows contact angle of water droplet on the surface before and after laser in air and water. The contact angle of water droplet on untreated surface is about 88°. Laser irradiation of surface with 50 mJ/cm\(^2\) and 45 pulses in air leads to a decrease in water droplet contact angle to 79°. With increasing the fluence to 120 mJ/cm\(^2\) contact angle increases to about 121.3°. The results are consistent with decreasing the peak intensity of the polar groups in IR spectrum. Removing the skin and interaction of the water with the porous surface also leads to increasing the water contact angle due to the presence of the air pockets which repel the water droplet from the surface.
For the samples irradiated in water the contact angle changed within a smaller range and a different manner. It increased slightly with irradiation at 50 mJ/cm$^2$ and then decreased at higher fluences. These results can be explained by difference in OH and CO peak intensities at various fluences since no morphological changes were observed for sample irradiated in water.

**Table 1.** The contact angles of water droplet on the samples

| Fluence (mJ/cm$^2$) | 0     | 50    | 85    | 120   |
|---------------------|-------|-------|-------|-------|
| Contact angle (°)   | In air| 88    | 79.6  | 84.2  | 121.3 |
|                     | In water| 88    | 90.2  | 86.7  | 84.6  |

3.4. Cell Culture Study and surface biocompatibility

Figure 4 shows the optical micrographs of cells cultured on the untreated and laser treated surfaces in the air and water. In our last paper we observed that the surface roughness is very important in cell adhesion to the PES film surface. The result of the cell culture in this experiment showed no significant increase on adhesion of the cell to the surface following irradiation of the membrane in air or water in spite of the increasing the surface roughness for samples irradiated at a fluence of 120 mJ/cm$^2$ in air. The number of adhered cells even decreases for membrane irradiated at a fluence of 50 mJ/cm$^2$ in water.

![Figure 4](image)

**Figure 4.** Optical micrographs of the cell cultured on (a) the untreated, and laser treated surfaces at fluence of 50 mJ/cm$^2$ (b) in air, (c) in water and at fluence of 120 mJ/cm$^2$ (d) in air, (e) in water.

In summary the cell adhesion is more for membranes irradiated in the air than in the water. However, the lack of toxicity of both of the samples to evaluate the biocompatibility in contact with the living environment is evident.
4. Conclusions
Laser processing in water, except to cool the material or to increase plasma pressure, it can also act as a chemical reagent. In this study, the surface of PES membrane was irradiated with XeCl laser in air and distilled water in the same condition. The interaction of light with the sample surface causes to vaporization of the surface material and a small amount of surrounding the target (in air or water). Then chemical reactions between the ablated species and molecules in the environment can occur. The link between environmental segregated particles such as O$_2$ molecules of the air or the OH stretching vibration of water molecules on the surface of the sample occurs. These peaks are observed in the IR spectra of both of them.

The irradiated samples in the water have higher peak intensity in the OH stretching vibration. The contact angle of the water droplet is decreased more for samples irradiated in water. The cell adhesion is also more for membranes irradiated in the air than in the water.

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