Laser surface modification of polyethersulfone films: effect of laser wavelength on biocompatibility

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Abstract

In this paper laser ablation of polyethersulfone (PES) films regarding to the change in biocompatibility of the surface is investigated at 3 different wavelengths of 193nm (ArF), 248 nm (KrF) and 308 nm (XeCl). The optimum laser fluence and number of pulses for the improvement of the surface biocompatibility is found by examination of the surface behavior in contact with platelets and fibroblasts cells at 3 wavelengths. These biological modifications are explained by alteration of the surface morphology and chemistry following irradiation. The results show that the KrF laser is the best choice for treatment of PES in biological applications.

1. Introduction

Polymers are being used in a wide range of applications, particularly in medical device industry. Understanding the surface characteristics of the polymer is important since the surface properties of materials in contact with biological systems play a key role in determining the outcome of biological interactions [1, 2].

Lasers are used as a standard tool for improving the biocompatibility of the surface [3–6]. Different materials are irradiated with lasers at different experimental conditions depending on the desirable results for various applications. Surface hydrophilicity of material is an important parameter in the medical applications. There have been remarkable advances in the understanding of the extraordinary wetting properties of rough surfaces which, contrary to the flat ones, can be tuned from superhydrophilic to superhydrophobic [7] opening up the possibility for many exciting applications [7–11]. Direct laser micro/nano structuring is a versatile method for controllable modification of materials’ surfaces [12–15].
Surface biocompatibility is influenced by the surface morphology, chemistry and specially wettability modifications, which should be investigated to account for the biocompatibility alterations. In this scope, contact angle measurement is a simple method for measuring the hydrophilicity of a surface. Different combinations of pulse numbers and fluence at each wavelength give rise to various microstructures and chemical modifications.

In our last papers [16-21] we investigated the effect of KrF, XeCl and ArF laser irradiation on the surface chemical, morphological and wettability of the polyethersulfone surface, individually. In this paper a brief comparison review between different wavelengths is done.

2. Methods and experimental procedures

PES films were prepared as described elsewhere [16-21]. They were cut into pieces of 80–100 μm in thickness and 30mm×10mm in dimension and were washed with ethanol before irradiation. PES samples were irradiated with ArF and XeCl lasers with pulse durations of ~25 ns. KrF laser was used at 3 pulse durations of 30 ns, 5 ps and 500 fs. The samples were irradiated with different number of pulses and fluences. Irradiation was done in ambient air and the central, fairly homogeneous area of the beam was selected for the observation of the chemical and morphological changes in the ns cases, while in the ultra-short irradiation a beam homogenizer was used in the experimental set up.

The laser-treated areas were characterized by field emission and scanning electron microscopy (FESEM & SEM). Chemical composition changes were investigated by Raman (λ = 473 nm, Nicolet Almega XR), attenuated total reflectance–Fourier transform infrared (ATR–FTIR, Thermo- Electron Nicolet 6700) spectroscopies. To characterize wettability, static contact angle measurements were performed by an automated tension meter, using the sessile drop method. A water droplet was gently positioned onto the surface using a microsyringe and images were captured to measure the angle formed at the liquid–solid interface. The mean value was calculated from at least five individual measurements. Successive measurements were reproducible within ±2°.

The number of adhered platelets was determined by LDH (lactate dehydrogenase) method [16, 17]; and cell culture studies were done using L929 mouse cells for investigation of the surface toxicity [16, 19].

3. Results and Discussions

3.1 Morphological changes
3.1.1 KrF laser irradiation

For the ns laser sources at all of the wavelengths, the morphology comprised irregular micro and nanosized features at low fluences and microcones at moderate fluences. In the case of KrF micro ripples at low (below the ablation threshold) and micro cones and columns appear on the surface at moderate and high fluences respectively. The number of cones increases with the number of pulses and their height with the irradiation fluence; until well-defined columns are formed on the surface at a fluence of 200 mJ/cm² [17].

On the other hand, the surface ablated with ps and fs pulses of KrF comprises microcones for all fluences used, while the roughness degree increases with the fluence. At the same fluence, the cone morphology and the roughness degree attained are more pronounced in the fs as compared to the ps case. Experiments performed at a different number of pulses for each pulseduration and fluence [17] indicate that the most probable mechanism behind microcones formation is the laser beam shielding by local inhomogeneities or surface instabilities induced by the laser irradiation process.

![Fig.1 SEM micrographs of the sample irradiated with a) KrF laser with 7000 (ns) pulses at 15 mJ/cm², b)1000 (ns) pulses of 100 mJ/cm² and c)1000 (fs) pulses of 150 mJ/cm²](image)

3.1.2 ArF laser irradiation

A threshold fluence of about 13±3 mJ/cm² was obtained for ArF laser ablation of PES [20]; then samples were irradiated at 7 mJ/cm² (below the ablation threshold) and 21 mJ/cm² above the ablation threshold. Ablation with 193 nm results in nanostructures at low and microbeads (or cones) at moderate fluences that become decorated with nanometric secondary protrusions at higher fluences (fig.2). Such nanostructures may be formed due to the re-deposition of the ablated photo-
fragments condensed on the surface between successive pulses, an effect which is often observed upon irradiation of polymers with ns pulses [22].

3.1.3 XeCl laser irradiation

The laser ablation threshold of PES was experimentally measured to be about 60 mJ/cm\(^2\) [21], and samples were irradiated at fluences of 25 and 50 mJ/cm\(^2\) (below the ablation threshold), and 70 mJ/cm\(^2\) in the range of the ablation threshold. XeCl laser interaction of PES has a thermolytical nature rather than direct bond disassociation because of low absorption coefficient of PES (about 120 cm\(^{-1}\)) at 308 nm. During XeCl laser ablation of PES, conical microstructures appear on the surface. The developed microstructures are laser fluence dependent as well as dose dependent, with the structures becoming more prominent with increasing pulse numbers. It is observed that at the fluence of 70 mJ/cm\(^2\), the material removal from the surface begins to start with about 300 pulses of laser irradiation [21]. This is because of the weak absorption of the PES at 308 nm that causes ablation to occur 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 was strongly absorbing at that wavelength.

On the other hand, irradiation of the samples below the ablation (at fluences of 25 and 50 mJ/cm\(^2\)), leads to formation of a microscopically smooth surface because of
melting and resolidification. The laser irradiated surface at 2 fluences regimes of below and above the ablation threshold is shown in Fig.3.

![SEM micrographs of the samples irradiated with XeCl laser](image)

**Fig.3** SEM micrographs of the samples irradiated with XeCl laser with a) 500 pulses of 50 mJ/cm² and b) 3000 pulses of 70mJ/cm²

### 3.2 Hydrophilicity alteration versus Chemical modifications

At all the wavelengths the increasing wettability were observed in the lower fluence regime, i.e. for fluences below the ablation threshold. CA minima indicated is associated with a change of thermochemical composition of the surface following KrF laser irradiation, particularly to the release of sulfonic and disulfonic acids of the type R–SO₂H (R = H, phenols) as well as carboxylic acids R–CO₂H (R = phenols, methyl, H): all are well known as surfactants and formed by the exposure of polyarylsulfones to UV light [23]. The presence of disulfonic acid is indicated by the ATR–FTIR spectra of the respective samples [18]. Above the ablation the surface chemistry changes especially carbonization with ns laser pulses which are observed in Raman spectra of the irradiated and non-irradiated surface leads to decreasing the hydrophilicity[17, 18].

The functional groups induced on the surface by ArF laser irradiation were examined with ATR-FTIR spectroscopy [20]. The spectrum shows a new peak at 1746cm⁻¹ assigned to (C- O group) appears with irradiation of the samples at the fluences of 7 and 21 mJ/cm². The peak intensity increases with increasing number of pulses at a fluence of 7mJ/cm². Laser irradiation up to3000 pulses produces radicals on the PES surface that are convertedto hydrophilic groups. Further irradiation leads to cleavageof chemical bonds and recombination of carbon radicals producing a surface with hydrophobic properties.
At a fluence of 21 mJ/cm², the peak is formed with lower pulse numbers (optimum numbers) and then disappears with 60 pulses. Material removal and cleavage of chemical bonds above the ablation threshold suppose to be responsible for the removal of radicals created on the surface with a slight increase in the number of pulses. The surface becomes very hydrophobic with increasing number of pulses. In the other word with increasing the number of pulses and the micro-cone formation, the presence of secondary nanofeatures onto microstructures may be responsible for the superhydrophobicity attained, since it is known that hierarchical roughness greatly enhances the wettability effects [3].

XeCl laser irradiation also can change surface chemistry or surface charge and leads to a change in water droplet contact angle on the surface. Although here the chemical changes are not pronounced as in the case of KrF and ArF laser irradiation. The chemical modification depends on the laser fluence and number of pulses. The most optimal condition for improving the hydrophilicity of PES surface is 500 pulses at a fluence of 25 mJ/cm² and it is believed to be a result of photo-oxidation on the irradiated surface. Further increase in number of pulses and fluence leads to cleavage of chemical bonds and recombination of carbon radicals and creation of hydrophobic properties on the surface [24]. On the other hand, at higher fluences with increasing the roughness, and under certain surface conditions, the contact angle increases. The laser fluence and number of pulses for minimum contact angle have been presented in table 1.

| Wavelength (nm) | 308 (XeCl) | 248 (KrF) | 193 (ArF) |
|-----------------|------------|-----------|-----------|
| Number of pulses| 100        | 7000      | 3000      |
| Fluence (mJ/cm²)| 70         | 15        | 7         |
| Minimum Contact angle obtained | 75°        | 16°       | 49°       |

### 3.3 Results for the biocompatibility tests

Two factors should be considered for cell adhesion on an irradiated surface: 1- chemical composition and 2- roughness due to structure formation or debris [16, 25]. According to the contact angle measurements, it seems below the ablation threshold; chemical changes of the polymer surface including oxidization in ambient air and creation of polar groups lead to increased cell adhesion [19, 25].
In order to quantify how the L929 cells reacted to the different surface topographies, the cell culture studies were done on the irradiated and non-irradiated surfaces and the number of cells was measured for each of the samples. The cell numbers were counted at several positions on the substrate in order to determine the standard deviation. It was shown that [19] the number of cells adhered on the surface irradiated at a fluence of 15 mJ/cm² of nanosecond KrF laser is increased significantly. Formation of the structures on KrF laser treated surfaces above the ablation threshold has no significant effect on cell adhesion. The cell adhesion is not changed even with increasing the hydrophilicity of the surfaces in this regime. On the other hand below the ablation, despite of increasing the surface hydrophilicity in all 3 pulse durations of KrF due to the chemical changes, the cell adhesion only is increased with the presence of the periodic nano structures on the surface irradiated with ns pulses.

The data from the LDH method on ArF laser irradiated surfaces show that the extent of platelet adhesion on PES films surface can be controlled by a change in the fluence and pulse numbers. The optimum pulse numbers and the fluence required to reduce platelet adhesion is 3000 pulses and 7mJ/cm² respectively (fig.4). This result was expected since the platelet adhesion decreases with an increase in surface wettability. Measurements of platelets adhered in the samples irradiated above the ablation threshold, showed a dramatic increase in platelet adhesion on the surface.

The platelet adhesion also decreases upon a XeCl laser treatment with various number of laser pulses below the ablation threshold. There is an optimum for number of pulses at each one of fluences to reduce platelet adhesion on the surface. The most optimal condition for decreasing platelet adhesion on the surface is a fluence of 25 mJ/cm² and 500 pulses (fig.4). On the other hand with irradiation of surface with 500 pulses at a fluence of 70 mJ/cm² the contact angle increases while the number of adhered platelet decreases [16]. Results of the cell culture studies show that fewer cells are attached on untreated surface in comparison to the laser treated ones. Increasing the surface roughness at a fluence of the 70 mJ/cm² increases the number of adhered cells to the surface.
4. Conclusions

Laser irradiation of polymers can change the surface biocompatibility. The extent and types of modifications depends on the laser parameters and the polymer. The values for absorption coefficient of PES are about $140$ and $6.1 \times 10^4 \text{ cm}^{-1}$ and $1.8 \times 10^5 \text{ cm}^{-1}$ at 308 and 248 nm and 193 nm respectively [11]. Regardless of the absorption of the surface at the laser wavelength, Irradiation of PES surface at the fluences below the ablation threshold, leads to increasing the surface hydrophilicity and biocompatibility especially for the decreasing the platelet adhesion in the blood contact works. It is observed that the wetting properties attained are mostly influenced by the photo-induced chemical changes, being highly dependent on irradiation parameters.

The results obtained from the cell-behavior studie son the PES surface revealed that the surface morphology or roughness is more important than the chemistry in cell culture on the surface. Nanoscale hydrophilic ripples appear on the surface following ns KrF laser irradiation significantly affect the adhesion of L929 cells on the surface.

In conclusion it is found that although the XeCl and ArF laser irradiation improve the surface biocompatibility and wettability of the surface, the KrF laser with middle absorption coefficient for PES (respect to the XeCl and ArF laser irradiation) can be supposed as the best wavelength for the improving the surface hydrophilicity.
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