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Effect of CO₂ pulsed laser irradiation on improving the biocompatibility of a polyethersulfone film

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Abstract

In this paper a 200 ns pulsed TEA CO_2 laser is used for treatment of polyethersulfone (PES) films surface. The laser induced structures and chemical compositions on the surface upon irradiation are studied. The hydrophilicity and biocompatibility of the irradiated surfaces are examined by contact angle and platelet adhesion measurements, respectively. The optimum number of pulses and fluence for improving the surface biocompatibility are found.

Key words: pulsed CO₂ laser, polyethersulfone film, contact angle, platelet adhesion

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1. Introduction

Polymers are widely used as biomaterials in medical applications. In order to enhance the biocompatibility feature, polymers surface should be modified with proper surface treatment techniques. A number of surface modification methods have been employed to achieve such ends. These include chemical treatment, plasma treatment, electron beam irradiation and laser irradiation [1-7]. Lasers can offer the user an exceedingly high degree of process controllability and flexibility.

Polyethersulfone is one of the most favorable polymers for hemodialysis membranes and thus improving its biocompatibility is essential if it is to be applied in blood contact works. Recently, some researchers have used laser irradiation for polyethersulfone film surface modification [8-12]. Pazokian et al have carried out laser treatment using excimer lasers at 193, 248 and 308 nm. They have shown that increasing the hydrophilicity of polyethersulfon (PES) surface leads to increasing biocompatibility in contact with blood. On the other hand the roughness is the most important parameter in cell culture on the surface and also, the biocompatibility is depended on the irradiation fluences [13-16].

In this work the effect of CO_2 pulsed laser irradiation on improving the blood compatibility and hydrophilicity of the PES film surface is studied.

2. Materials and methods

2.1. Sample preparation

The samples (PES,Ultrason E6020, Mw=58000, flakes) were supplied by BASF Co. PES was compressed at 250 °C and 30 Mpa ,using a laboratory press (Mini Pestpress,10 poyosciti), into pieces of about 80-400 μ m in thickness and 10 mm× 20 mm in dimension. The surfaces of all samples were ultrasonically washed in bath with methanol before irradiation.

2.2. Laser treatment

The samples were irradiated using a line tunable pulsed TEA CO_2 laser at the wavelength of 9.58 μ m. The laser was operated at the laser fluence of 150-400 mJ/cm² and repetition rate of 1-5 Hz.

2.3. Sample Characterization

2.3.1. Contact Angle Measurement

Hydrophilicity was evaluated by measuring the static water contact angle. Static contact angles were measured using the sessile drop method by a contact angle goniometer (Kruss G10).

All water drop contact angles are the mean value of five measurements on the surface \pm standard error ($\theta \pm 2^{\circ}$).

2.3.2. Platelet Adhesion Measurements

Human blood was collected into the 250 ml blood bag. The blood was centrifuged to obtain platelet rich plasma (PRP). The PRP concentration was determined by a Cobas blood counter and used to normalize all the experiments. The PRP was placed on PES films of 1cm² area and kept for 1 h at 37 °C. Then the films were taken out and dip-rinsed twice with phosphate buffer saline solution (PBS) in order to remove the platelets that were not attached to the film. The number of adhered platelets was determined by lactate dehydrogenase (LDH) method [17]. The films were put in 5 ml of PBS containing Triton- X100 for 1 h at room temperature to lyse the adhered platelets.

The LDH activity of lysate was measured with an enzymatic method in which the adhered platelets were counted using a calibration curve of platelet counts. The change in ultraviolet absorption at 340 nm was measured using a spectrophotometer. The platelet adhesion test was repeated three times using different PRP and the mean value was obtained.

3. Results and Discussion

3.1. Contact-Angle Changes

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Contact angle measurement is a simple method for investigation of the hydrophilicity of a surface [18].

Table1. Shows the contact angles measured on the irradiated surfaces with 2000 pulses at the repetition rate of 4 Hz and different laser fluences.

 Table 1.Contact angle of water droplet on untreated and laser-treated surfaces with different laser fluences with

 2000 pulses

Fluence	0 mJ/cm^2	170 mJ/cm ²	200 mJ/cm ²	225 mJ/cm^2	250 mJ/cm ²	300 mJ/cm ²
Contact angle(degree)	79	67.53	68.90	63.20	72.60	74.70

As it is indicated in this Table, the surface wettability tends to increase with increasing the laser fluence; the contact angle reaches a minimum value and then increases with further increases in the fluence. The fluence at which the contact angle becomes minimum (F_{min}) is subthreshold fluence (the threshold fluence is found experimentally to be ~ 250 mJ/cm²). Irradiation with fluences above F_{min} always causes a decrease in surface wettability (increasing contact angle) due to the cleavage of chemical bonds (Fig. 1). As well know, Oxygen containing group on polymer surfaces are responsible for the change of surface hydrophilicity [17-19], then by controlling the laser fluence , the surface could be modified as polar or non-polar.

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F=300 mJ/cm²

F=250 mJ/cm²

F=225 mJ/cm²

Fig.1-The images of the water drop on PES surface at different laser fluences and 2000 pulses.

Figure 2 shows the contact angle on the surface as a function of pulse numbers at the fluence of 225 mJ/cm^2 and repetition rate of 4 Hz.

As it is shown in this figure, the contact angle initially decreases with increasing number of pulses up to 5000 pulses and then increases with further pulses.



Fig.2-Dependence of the contact angle of the pulsed TEA CO_2 laser irradiated PES films as a function of pulses number at the laser fluence of 225 mJ/cm²

It seems likely that the - oxidized groups would be decomposed with further pulses (more than 5000). The images of the water drop on PES surfaces at different number of pulses are shown in figure3.

3.2. Platelet Adhesion

N=2000

To test the thrombogenecity of PES surface the LDH method was used. This method provides a quantitative determination of the number of platelets adhering to the surface and providing procoagulant sites [19,20].

Figure 4 shows platelet adhesion as a function of pulse numbers. As can be seen in the figure, the optimal laser pulses required to reduce the platelet adhesion is 1000 pulses at a fluence of 225 mJ/cm^2 .



N=0



N=1000

Fig.3-The images of the water drop on PES surface irradiated with different laser pulses number and the fluence of 225 mJ/cm².

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Fig.4- Number of platelet adhered to the surface as a function of number of laser pulses at fluence of 225 mJ/cm².

Laser treatment of polymers introduces specific chemical groups onto the surface that not only increase the wettability on the surface but also have a specific effect on the interaction of platelets with surface.

The radicals formed on the CO_2 laser irradiated PES surface are modified into corresponding peroxides in contact with air.

4. Conclusions

In this work, the effect of pulse numbers and the fluence of a pulsed TEA CO_2 laser irradiation on the biocompatibility of PES were investigated. The results showed that, irradiation below the ablation threshold (at fluence 225 mJ/cm² and 5000 pulses) increases the surface wettability. The obtained results also indicated that, at the fluence of 225 mJ/cm² there is an optimum for number of pulses to reduce platelet adhesion on the surface. Therefore by controlling the laser fluence 21st International Laser Physics Workshop

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and number of pulses, the surface could be modified for manners of polar groups or non-polar groups. It concluded that wettability and platelet adhesion are related to surface chemistry.

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