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Wetting ability modifications in biocompatible polymers induced by pulsed lasers

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Abstract. Wetting ability was measured in the surface of different biocompatible polymers, such as mylar, polyethylene, poly-methyl-methacrylate and teflon. Nanosecond pulse lasers at intensities of the order of 10^8 W/cm² were employed at different doses to irradiate the polymeric surfaces and to induce wetting ability modifications due to the chemical and physical surface changes vs. irradiation time and laser wavelength. In particular, the contact angle as a function of the surface roughness was investigated, as will be presented and discussed.

1. Introduction

In the field of Biomaterials it is important to know the wet ability and the roughness of the material to be implanted in the human environment [1, 2]. Polymeric materials have hydrophilic and hydrophobic behaviour, however their original properties can be strongly modified using surface treatments such as the high intensity laser irradiation. The laser treatments may change the surface temperature, inducing scissions, cross-linking and chemistry activity, modifying roughness and hardness and developing new surface properties depending on the irradiation conditions. In this work we study the changes and the dependence of the wet ability of polymeric materials subjected to irradiation of pulsed lasers as a function of the laser properties, i.e. as a function of the amount of energy released to the material.

2. Materials and Methods

The polymers used in this work are: Mylar (C₁₀H₈O₄)_n, polyethylene (-CH₂-), polytetrafluoroethylene (-CF₂-) and polymethylmethacrylate ((C₅O₂H₈)_n). A Q-switched Nd: YAG laser, operating at the fundamental wavelength of 1064 nm (IR), with pulse duration of 3-9 ns, energy of 180 mJ-300 mJ, spot diameter Ø 3mm in diameter has been used at the Department of Physics of Messina. The ArF excimer laser operating at the fundamental wavelength of 193 nm (UV), also beam energy of 160mJ, pulse duration of 18 ns, spot diameter Ø 2mm was employed at the Department of Surgical Specialties, UOC of Ophthalmology of Messina. The excimer laser KrF, operating at the fundamental wavelength of 248 nm, beam energy of 165mJ, pulse duration of 25 ns, spot diameter Ø 8mm has been used at the Department of Physics of Lecce. A surface profiler Tencor P-10 using whit a 1 mg tip force, scansion length of 500 mm and scan speed of 100 µm/s was employed at the at the INFN-LNS



of Catania to perform roughness measurements [3]. The technique of the sessile drop, consisting in the measurement of "contact angle" between the tangent to the profile of a drop, deposited on the sample surface, was employed.

The experimental setup which allows direct measurement of the contact angle consists of four elements: a mobile platform that houses the sample; an optical microscope; a webcam interfaced to a computer; a calibrated syringe that allows to deposit on the surface of the drops of liquid samples. Distilled water (1 μl) and physiological solution (1 μl) were used as test liquid. The contact angle θ (degree) was calculated from the height h (mm) and the base diameter d (mm) of the droplet itself [4] as in equation:

$$\theta = 2\arctg\left(\frac{2h}{d}\right) \quad (1)$$

Liquids wet surfaces when their contact angle is less than 90° .

From surface profiles it is possible to determine the surface vertical and horizontal roughness (Fig. 1).

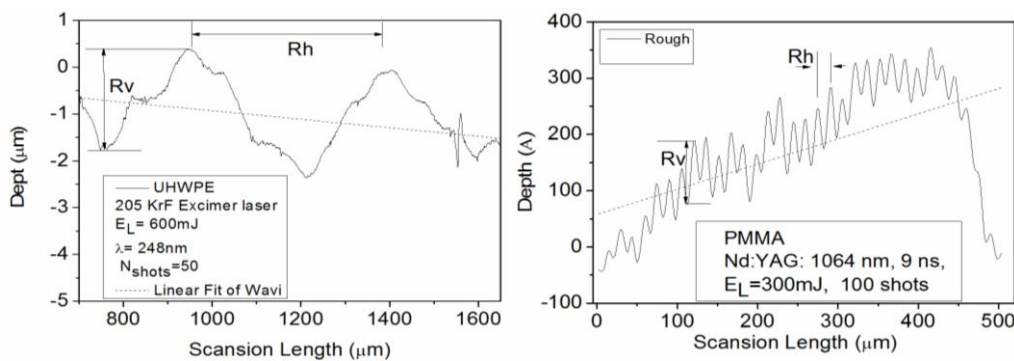


Figure 1. Vertical and horizontal Roughness.

Assuming as axis the average line of the profile, the average vertical roughness R_v depends on the vertical dimension y_i of the profile with respect to the average line as equation (2):

$$R_v = \frac{1}{n} \sum_{i=1}^n |y_i| \quad (2)$$

3. Result and Discussion

PMMA was irradiated in air with Nd:YAG and excimer laser. The laser energy was changed from 60 mJ to 180 mJ for IR irradiation and from 60mJ to 160 mJ for the UV ablation. The number of laser shots was 60 (Fig. 2.a,c). PMMA was also irradiated maintaining the maximum energy constant and varying the number of laser shots (Fig. 2.b,d). The contact angle of distilled water on the pure PMMA is approximately 77° . The action of UV laser decreases the angle of wet-ability making the PPMA hydrophilic, while the lasers in the IR increases the wetting angle making the PMMA hydrophobic [5-6]. The variations of the angle due to the surface wettability may be due to changes in surface morphology. PMMA and UHMWPE were irradiated in air with the Nd:Yag laser maintaining constant the energy ($E_L=300$ mJ) and by varying the number of laser shots. By the graphs of Fig. 3 it is clear that both polymers show an increment of the wettability by increasing the vertical and horizontal roughness R_v and R_h , making the materials more hydrophobic. Mylar and PTFE were irradiated in air with the laser Nd:Yag at the maximum energy ($E_L=300$ mJ) and by varying the number of laser shots. The graphs of Fig. 4 show that for both samples, initially hydrophobic, the contact angle first decreases and then increases with the roughnesses R_v and R_h and making them hydrophilic. PMMA and UHMWPE were irradiated in air with the two different excimer lasers ($\lambda=193\text{nm}$ and $\lambda=248\text{nm}$)

at energy $E_L=165$ mJ and $E_L=300$ mJ, respectively, and varying the number laser shots (Fig.5). The graphs show a linear reduction of the wettability as a function of roughness R_v and R_h . Experimental results demonstrate that the action of UV laser change the surfaces from hydrophobic to hydrophilic.

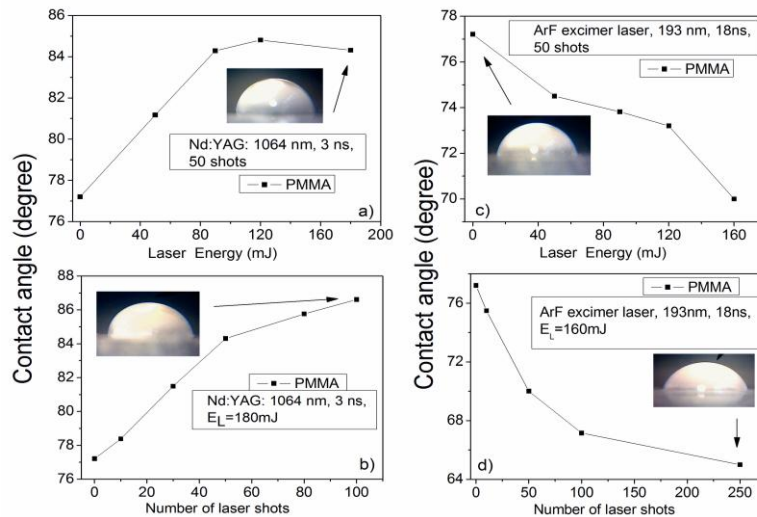


Figure 2. Contact angle of PMMA vs. IR laser energy (a) and IR number of laser shots (b) and UV laser energy (c) and UV number of laser shots (d).

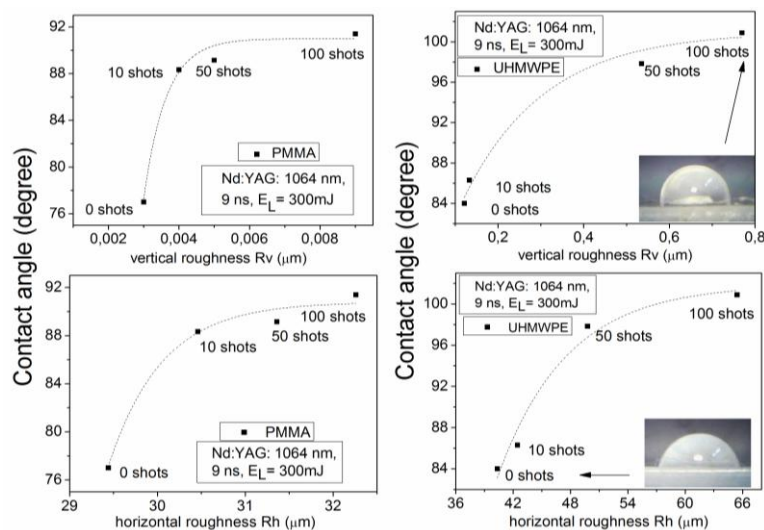


Figure 3. Roughness vertical and horizontal of the materials PMMA and UHMWPE before and after the irradiation with the laser of Nd:YAG.

3. Conclusions

The results obtained reveal that the surface modifications change the values of wet ability by increasing or decreasing the contact angle both of the distilled water and physiological solutions. The roughness created by laser irradiation increases or decreases the angle of wettability making the investigated material hydrophobic or hydrophilic i.e. controlling an important biocompatibility factor in the preparation of biomaterials and prosthesis. By varying the photons energy and the laser properties, the surface polymer modification can be controlled. This result is extremely important in

the medical field because it means to improve the biocompatibility and the functionality of biomaterials and functional prostheses. For example, the surfaces of the materials used for the mechanical valve prostheses and therefore in contact with the blood, as it coagulates on rough surfaces (hydrophobic surfaces: low wettability), must be smooth and polished to facilitate removal of microscopic thrombotic formations before they reach dangerous proportions. Instead, in the artificial valve prosthesis (made with fabrics of polymeric fibers) is important to promote clotting within the porous wall of the prosthesis in order to avoid or limit the loss of blood.

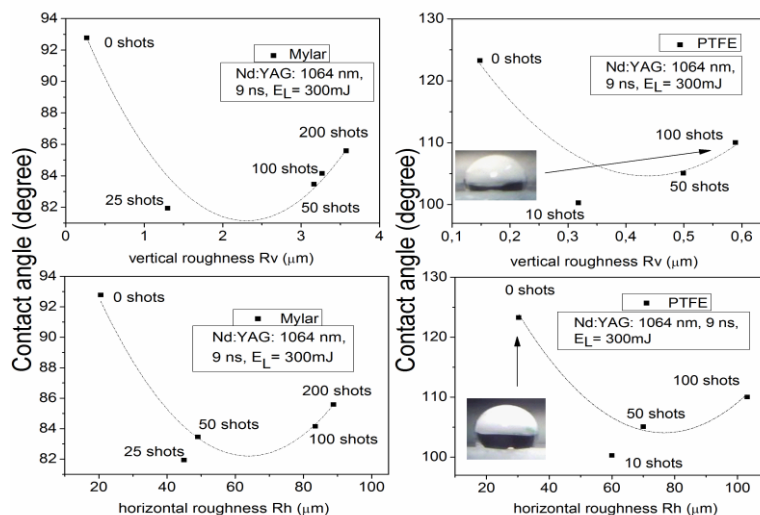


Figure 4. Roughness vertical and horizontal of the materials Mylar and PTFE before and after the irradiation with the laser of Nd:YAG.

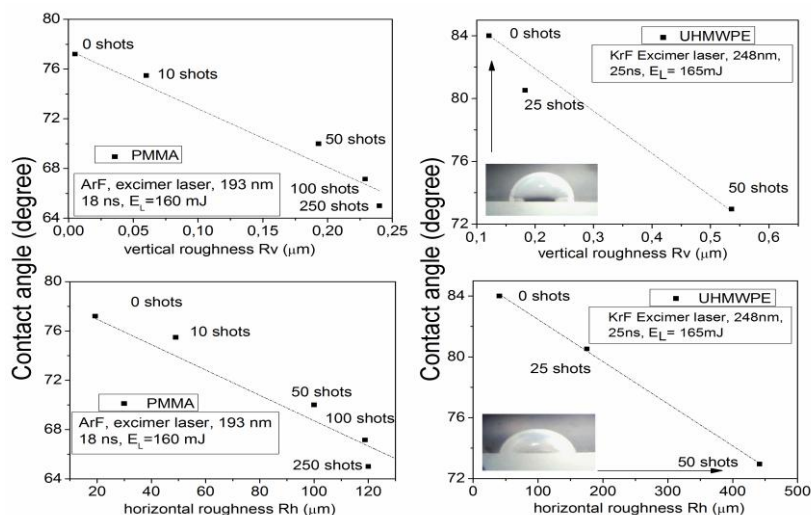


Figure 5. Roughness R_v and R_h of PMMA and UHMWPE before and after the irradiation with the different excimer lasers ($\lambda=193\text{nm}$ & 248nm).

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