A Liquid contact angles on biocompatible surfaces

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Abstract

Measurements of liquid contact angles on biocompatible surfaces have been performed at the Physics Department of Messina University. Biological solutions, polymers, ceramics and metals have been studied.
Surface treatments by using different laser irradiations, depending on the laser intensity and wavelength, permit to change drastically the wet-ability of many materials and to enhance their biocompatibility and functionality.
Results of our investigations put in evidence the best materials to increase or to reduce the wet-ability of the biological liquids. Results will be presented and discussed in detail with special regard to their applications in biological environment where the materials can be embedded.

Introduction

The degree of biocompatibility of a material is a function not only of the characteristics and properties of the materials and implanted devices, but also of the conditions of the host organism and of the surgical technique. It is important to know the wet-ability of the material to be implanted in order to determine whether or not it should promote the epitaxial cells growth in the body [1]. The wet-ability is a very important property of surfaces and can be defined as the ability to wet uniformly and in a stable manner from a liquid substance [2-3].
The ablation with laser pulses is a high-precision technology and spatial resolution which allows to obtain an efficient energy transfer without significantly damaging the surrounding material. A characteristic advantage of this technique is its ability to modify the properties of wet-ability of the substrate [4].

Materials and methods

In this work were measured and compared the angles of wet-ability of polymeric substrates, metallic and ceramic biocompatible materials [5]. The main polymers used for the calculation of wet-ability in this work are: *Intraocular lens AcrySof IOL (PMMA based), polyethylene (PE), polytetrafluoroethylene or teflon (PTFE), polylactic acid (PLA), polymethylmethacrylate (PMMA)*.
At the Department of Plasma Physics of the University of Messina has been used a Q-switched Nd: YAG laser at intensity of 10^8 W/cm^2 operating at the fundamental

wavelength of 1064 nm, with pulse duration of 3 ns, energy of 180 mJ, which can operate in single shots and repetition rate (1 to 10 Hz).

At the University Hospital of Messina in the Department of Surgical Specialties, UOC of Ophthalmology was used the UV-ArF excimer laser (Technolas 217Z100P) operating at the fundamental wavelength of 193 nm, characterized by a beam energy of 160 mJ with pulse duration of 18 ns with a Gaussian energy profile plate, working in single mode or repetition rate of 100 Hz.

At the Dental Clinic of Catania has been used a diode laser (Lamba Scientific - D5-Doctor Smile) fundamental wavelength 810 nm, 5 W, CW.

Metallic materials from equipment used for measuring wet-ability in this work are *Gold, Silver, Palladium, Copper, Titanium, Austenitic Steels AISI 304 and AISI 316L and Titanium Alloy* Ti_6Al_4V *(TAV), Zinc (Zn).*

The ceramic materials of which has been calculated the angle of contact are: Al_2O_3, *Diamond*, SiO_2, *Glassy Carbon (CVD), Silica*, TiO_2.

The method used for the measurement of the angles of wet-ability involves the measurement of the profile of a drop of liquid at rest on a solid surface. This method, called *sessile drop* [2,3], consists in measuring the "contact angle" between the tangent to the profile of a drop, deposited on the sample surface, and the surface itself.

Figure 1: sketch of the experimental setup built for the measurements and calibrate syringe.

The contact angles of drops of liquid (deposited on the surface by means of a calibrate syringe) were measured in a direct way by means of a webcam Philips CamSuite 2.0 aligned to the eyepiece of an optical microscope that records video images and pictures of the system formed by the solid sample and drop (Figure 1). Golden Ratio is a PC code based on a transparent mask to be placed over an image on the screen. Is serves to analyze the image, while the axes instead can be used for measuring angles and lengths (Figure 2).

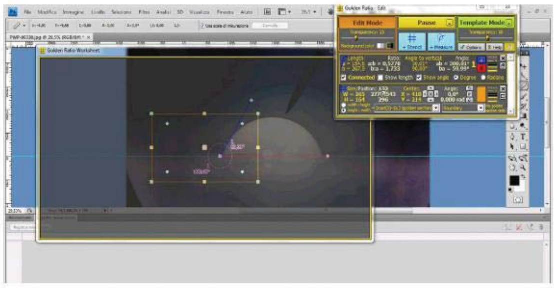

Figure 2: transparent mask software Golden Ratio to be placed above the picture on the screen.

The samples are cleaned on the surface with alcohol and are dried with a stream of dry air. It good that the sample is always dry when you deposit the drops. As test liquid was used 1 µl of saline solution. The measurements were carried out at room temperature (T=22°, U.R.=35%, P=1atm) and for each material were made 6 measures, of which the average is calculated (Figure 3).

Measurement of wet-ability [3]: The contact angle was calculated by the size of the droplet itself. For very small droplets the effect of distortion of gravity is minimal and the droplet can be seen as the clove of a sphere. The contact angle ϑ (*degree*) was calculated from the height *h* (*mm*) and the base diameter *d* (*mm*):

$$\theta = 2arctg(\frac{2h}{d}) \qquad (1)$$

for $\vartheta < 90°$, and

$$\theta = 90^\circ + \cos^{-1}\frac{4hd}{4h^2 + d^2} \qquad (2)$$

for $\vartheta > 90^\circ$.

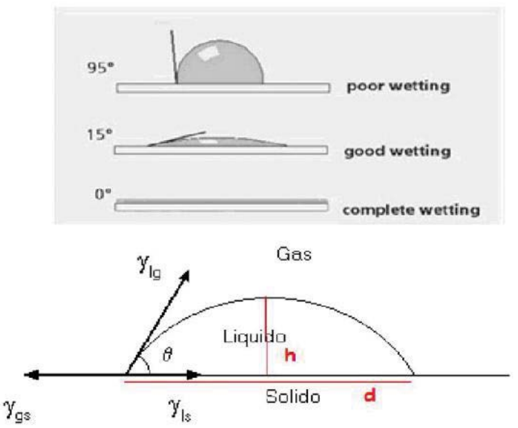

Figure 3: variation of wet-ability and variation of wet-ability and determination of the contact angles

One of the main objectives in *Endodontics* you achieve optimum cleaning of the root canal system through use of a "rational" of endodontic instruments and solutions for irrigation. The list of available solutions to be used inside the channels is: saline, the calcium chelators (*E.D.T.A. PLUS, E.D.T.A. 17%*), sodium hypochlorite (NaOCl) at various concentrations (*NICLOR5, HYPOCLEAN*) and water [6].

Results

We irradiated the PMMA with three different sources by varying initially the laser energy from 60mJ to the maximum energy (180mJ for the Nd: YAG laser and 160 mJ for the Technolas) for 60 shots and then instead, keeping to the maximum energy constant and varying the number of ns laser shots from 10 to 250. With the laser diode we irradiated to the sample maximum energy for different times (5 to 10 minutes). The variations of the surface wet-ability of PMMA after the laser treatments are reported in Figure 4.

The variations of contact angles of polymeric metallic and ceramic surfaces are shown in the figure 5.

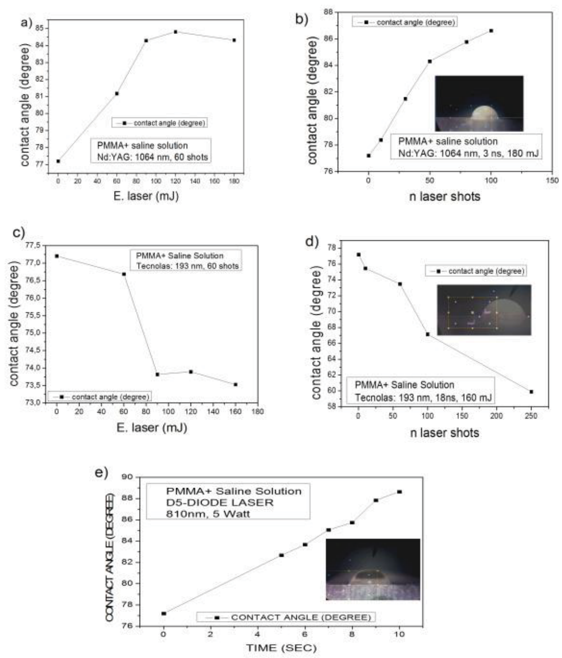

Figure 4: a) Trend contact angle of PMMA vs. energy Nd:YAG laser (60mJ - 90mJ - 120mJ - 180mJ); b) Trend PMMA contact angle vs. n laser shots Nd:YAG (10, 30, 60, 80, 100); insert: angle contact PMMA-Nd:YAG - 100 laser shots; c) Trend contact angle of PMMA vs laser energy Technolas (60mJ - 90mJ - 120mJ - 160mJ); d) Trend PMMA contact angle vs. n laser shots Tecnolas (10, 60, 100, 250); insert: contact angle PMMA-Technolas - 250 laser shots; e) Trend contact angle vs. time PMMA laser pulse D5-Doctor Smile (5', 6', 7 ', 8', 9 ', 10'); insert: contact angle PMMA- D5-Doctor Smile – time pulse shots 10 minuts.

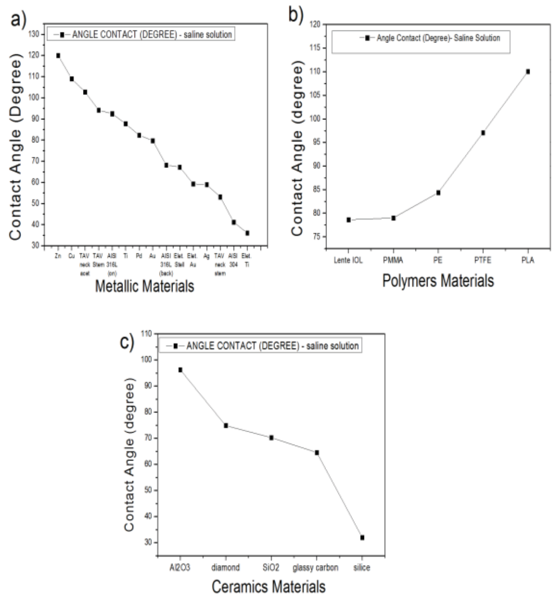

Figure 5: angle contact of a) polymer materials b) metallic and c) ceramic.

The variations of the contact angle of Polyethylene (PE) to the different percentages of concentrations of Fe2O3, Methylene Blue (B.M.) and Carbon Nanotubes (CNT) are shown in Figure 6.

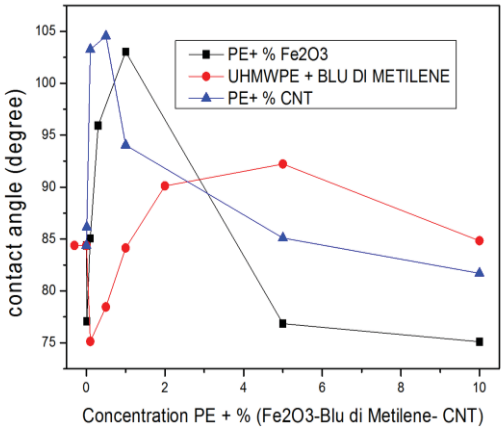

Figure 6: contact angle of PE at different percentages of concentrations: Fe2O3, B.M., CNT.

The variations of the contact angles of PMMA and of dental tooth of irrigants tested and the calculation of the relative surface tensions are shown in the figure 7.

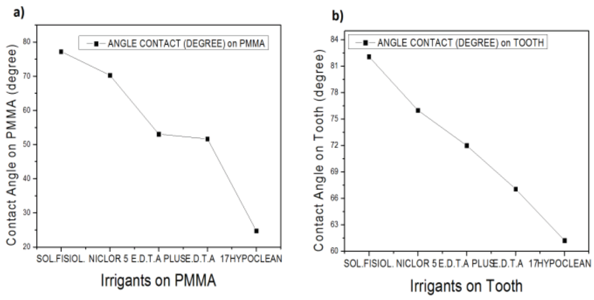

Figure 7: contact angle of dental irrigating a) PMMA, on b) tooth.

Discussion and Conclusion

The contact angle on the pure PMMA surface on which it was resting the drop for saline solution is approximately 77°. After irradiation by the Nd: YAG laser an incremental of about 7° or 10° is measured. The contact angle to 180mJ for 60 shots is about 84°, and for 100 shots laser and energy of 180 mJ is about 87° (see Figure 4 (a,b)). After irradiation through the Technolas of wavelength 193 nm, PMMA showed a change in wet-ability of the surface. The contact angle decreases by about 4° or 17°, explainable value considering the fact that ultraviolet light induces photochemical and photo thermal effects [7,8] and that the polymer PMMA is not very permeable to UV rays. The contact angle to 160mJ for 60 shots is about 73°, and for 250 shots laser and energy of 160 mJ is about 60° (see Figure 4(c,d)). The irradiance from the D5-Doctor Smile of wavelength of 810nm allows to modify the surface of the PMMA and thus increase its wet-ability with a contact angle of about 12° to irradiation times of the order of ten minutes. The contact angle after irradiation 5W of 10 minutes is about 89° (see Figure 4-e).

As regards the metals the metal more hydrophobic (> 90 °) is copper with a contact angle of 109°. Poorly wettable is also the titanium alloy of the neck of a hip prosthesis which is inserted into the acetabulum (θ=103°), while the opposite part of the neck that must namely be introduced in the stem is hydrophilic (<90°) has a contact angle of 53° capable of forming chemical bonds directly with the bone tissue, but also with the soft tissues of living organisms. The humeral nail and the bone plate is made of stainless steel AISI 316L (θ=94°) (see Figure 5-a). Among ceramic materials analyzed, alumina is the most bioinert, characterized by a high chemical-physical environment biological showing a contact angle of 96°, while the silica is very wettable with a contact angle of 32° (see figure 5-b). Among the polymeric materials examined the biocompatible material that the highest value of the contact angle, hydrophobicity index, is the PLA (θ=110°), while the IOL AcrySof intraocular lens has a small contact angle (θ=79°, hydrophilic) particularly important in relation to the maintenance of the tear film, the maintenance of which is a necessary condition for compatibility between the eye and the lens. (see Figure 5-c).

Figure 6 shows the trend of polyethylene (PE) at different concentrations of Fe_2O_3, Methylene Blue (B.M.) and Carbon Nanotubes (CNT). The concentrations of Fe_2O_3 were added in PE with the percentage of 0.01% - 0.1% - 0.3% - 1% - 5% - 10%. Concentrations of Methylene Blue (B.M.) were added in PE with the percentage of 0.1% - 0.5% - 1% - 2% - 5% - 10%. Concentrations of Carbon Nanotubes have been added in the PE with the percentage of 0.01% - 0.1% - 0.5% - 1% - 5% - 10%. These impurities give the surface of the PE different optical properties and therefore a significant variation of the contact angle. In fact, the contact angle of the untreated PE is of θ=84°.

The wet-ability of the polyethylene can therefore be suitably varied by adding different concentrations of Fe_2O_3, BM, and CNT with the possibility to make the hydrophobic PE (θ <90°) or hydrophilic (θ>90°) depending on the need (for example , to promote epitaxial growth or to its inhibition).

In the figure 7 (a-b) is shown the trend of the variation of the angle of contact of the endodontic irrigants used in dentistry of PMMA and of the tooth. The contact angles of irrigants on PMMA are respectively found: NICLOR 5 (θ=70°); E.D.T.A PLUS (θ=53°); E.D.T.A 17% (θ=51°); HYPOCLEAN (θ=25°). The contact angle of irrigants on the tooth are: NICLOR 5 (θ=75°); E.D.T.A PLUS (θ=72°); E.D.T.A 17% (θ=67°); HYPOCLEAN (θ=61°). The contact angle measurements may be influenced by a number of factors, including surface preparation, contamination, the environment, the temperature and the size of the droplet. The contact angles may increase or decrease as the temperature changes and do not change dramatically with it. The variations in surface wet-ability may be due to changes of roughness and / or modifications of the chemical properties of the surface. The action of the environment is generally determined by the absorption of vapour on the polymer surface, effect which reduces the surface tension. As reference liquid for the measurement of the angle of wet-ability in addition to the physiological solution and distilled water were considered four endodontic irrigants commonly used in dentistry. It has been found that the use of endodontic irrigants to have the very low surface tension and that the wet-ability of the solution governs the capacity of its penetration in both the main and side channels, and in the dentinal tubule. Expect to deal with the biocompatible materials as well as with the laser also with the processes of ion implantation, thermal and chemical processes in order to modify the surface properties. To change the internal properties of the materials we will send beams of electrons and gamma rays.

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