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Published by IFSA Publishing, S. L., 2022
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Study of Polycarbonate Wettability and its Antibacterial Properties after Excimer Laser Irradiation at the Ablation Threshold Fluence

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Received: 2 June 2022 /Accepted: 4 July 2022 /Published: 29 July 2022

Abstract: Wettability is reported to be one of the most important factors in bacterial attachment into the surface. Superhydrophobic surfaces show the lowest bacterial adhesion. In this paper, effect of an excimer laser irradiation at the ablation threshold fluence with different number of pulses on the wettability and antibacterial properties of polycarbonate samples was investigated. Sessile drop method and gram staining technique were used for water contact angle measurement and adhered bacteria identification respectively. Laser irradiation on the polycarbonate surface, cause intense changes in its wettability. High number of laser pulses at the ablation threshold fluence, followed by suitable hierarchical micro-nano structures fabrication on the surface, causes super water repellent surface fabrication. This fabricated surface shows superhydrophobicity and antibacterial properties and can be used in many applications such as medical devices, water and food industry. Field Emission Scanning Electron Microscopy was used for investigating the morphology of the superhydrophobic fabricated polycarbonate and to ensure adhered bacteria rate of the superhydrophobic sample.

Keywords: Antibacterial properties, Excimer laser, Polycarbonate, Superhydrophobicity, Wettability.

1. Introduction

Colonization and bacterial attachment on the surface of medical devices cause bacterial infections and threats to human health [1]. As the use of antibiotics, there are several approaches to kill the bacteria directly [2], but increasing the bacterial resistance to antibiotics followed by the emergence of new strains of drug-resistance bacteria, reduces the tendency to use these methods [3].

On the other hand, there are other techniques to prevent bacterial infections such as some metal particles using. Metal surfaces such as silver or copper have shown antibacterial efficacies that may control bacterial infections [4], but using this method leading to irreversible destructive effects such as DNA molecules damage [5].

Using new methods based on preventing the initial adhesion of bacteria to the surface, does not have the destructive effects of previous methods and also the antibacterial effect is more lasting. These surfaces can reduce the adhesion force between bacteria cells and the surface to enable the easy removal of bacteria before a biofilm formation [6].

Antibacterial surfaces have attracted scientists attention in the last decades [7, 8] due to their extensive applications such as industrial equipment, human health, food and water industry. As was mentioned in the previous paragraph, these surfaces prevent the initial bacterial attachment to the surface and subsequently biofilm formation [9].

Multiple physical aspects of the material including wettability, roughness, surface charge and energy have been considered to influence on the bacterial adhesion rate, but wettability is reported to be the most relevant parameter for bacterial adhesion control [10]. Superhydrophobic surfaces have been reported to show the lowest adhered bacteria due to their micro-nano structures [11]. There are several methods for superhydrophobic surfaces fabrication including chemical etching [12], solution immersion [13] and laser processing [14].

Laser irradiation can change the surface wettability due to the chemical changes and micro/nano structures formation on the surface and is one of the most effective techniques for superhydrophobic surfaces fabrication. Numerous articles have been published investigating the effect of the laser irradiation at fluences of above the ablation threshold on the wettability of the sample [15]. In this paper, effect of an excimer laser irradiation of polycarbonate at the ablation threshold fluence on its wettability is investigated. Due to laser processing, at these fluences and with high number of pulses, the surface is changed to superhydrophobic one. Finally, the bacterial adhesion rate on the irradiated sample is tested.

2. Experimental Method

2.1. Experimental Work

Polycarbonate is one of the most widely used polymers in food and medical industries. For example, this polymer has been used in blood filters and blood reservoirs for more than 20 years. In addition, this polymer is also used in food packaging containers. These applications are directly related to human health. Therefore, it seems that antibacterial polycarbonate fabrication is very essential.

Polycarbonate samples with the thickness of 1mm were cut into length and width of 1cm × 1cm. The samples were washed with water and alcohol to be cleaned before laser processing. The UV-Vis spectrum of the selected polycarbonate is shown in Fig. 1.

As it can be seen from the spectrum, PC has high absorption at the UV range of the spectrum.

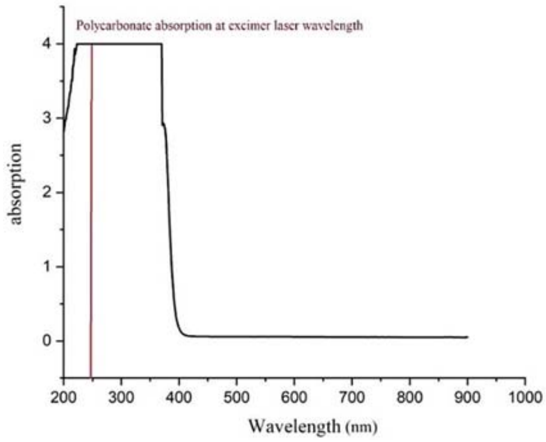

Fig. 1. UV-Vis spectrum of polycarbonate.

The single pulse laser ablation threshold can be obtained from the extrapolation of the graph of laser ablation rate vs laser fluence [16]. The fluence for the single pulse ablation threshold of PC samples in 248 nm was obtained to be about 40 mJ/cm^2. For investigating the effect of the laser irradiation on the polycarbonate wettability, samples were irradiated by a pulsed KrF laser with 25 ns duration and 248 nm wavelength at the fluence of 35 mJ/cm^2 (very close to the ablation threshold) with different number of pulses. The experimental setup is shown in Fig. 2.

The contact angle of the pristine and irradiated samples were realized by sessile drop method. Field Emission Scanning Electron Microscopy (FESEM) was used for investigating the changes in the superhydrophobic fabricated surface's morphology.

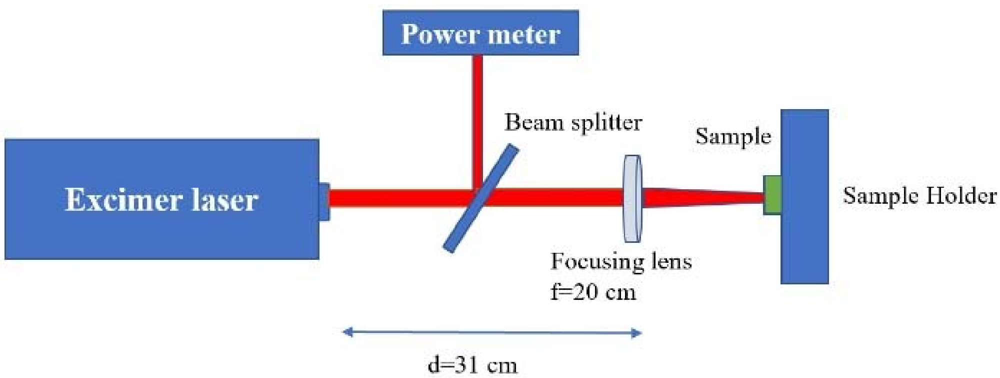

Fig. 2. Scheme of the experimental setup.

2.2. Bacterial Retention

E-Coli bacteria culture was inoculated into 4 mL LB and then incubated at 37 °C to an OD_{600} of 0.5. The culture was diluted 1:3 in sterile phosphate buffer solution (PBS). 500 microliters of diluted bacteria cultures were added to each well of polycarbonate samples. After washing with PBS, bacteria were fixed on the samples with 4 % paraformaldehyde in PBS for 30 min at room temperature and then Samples were rinsed with PBS. Finally, Gram staining was done.

One of the practical methods for identification of bacteria, is gram staining. Bacteria are classified into two categories based on their colour after gram staining test. Gram-negative and gram-positive bacteria are violet and red colour after gram staining.

In this paper, the superhydrophobic fabricated sample and the pristine were tested for E-Coli bacteria adhesion with gram staining method. E-Coli bacteria is gram-negative and can be identified easily in optical microscope due to its violet colour after bacteria culture and gram staining test.

3. Results

3.1. Wettability

Fig. 3 shows the changes in water contact angle of the samples irradiated at the fluence of 35 mJ/cm^2 and with different number of pulses.

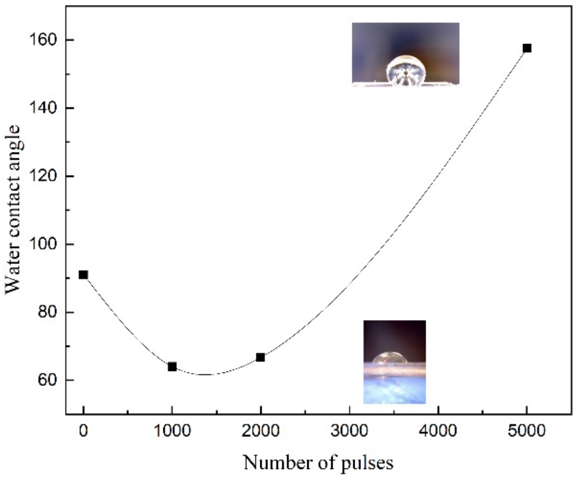

Fig. 3. Water contact angle of the irradiated polycarbonate samples at the fluence of 35 mJ/cm^2 with different number of pulses.

As it can be understood from the figure, following irradiation of the samples at this fluence with 1000 and 2000 number of pulses, the surface become hydrophilic, while the irradiated polycarbonate shows superhydrophobic behavior with 5000 pulses of irradiation.

3.2. Bacterial Adhesion Test

As was mentioned in Section 2.2, after bacteria culture, gram staining method was used for the superhydrophobic fabricated sample and the pristine. All the samples with bacterial culture and gram staining tests, were washed with phosphate buffer solution (PBS) before taking microscopic images. Therefore, only adhered E-Coli bacteria can be seen in the microscopic images.

Fig. 4 shows the microscopic images of these samples for E-Coli bacteria identification. As it can be seen from the figure, adhered E-Coli bacteria can be seen easily on the pristine sample while almost no bacteria can be identified on the superhydrophobic one. This means that the superhydrophobic fabricated sample is also antibacterial. Water droplet, can be slipped easily on the superhydrophobic surfaces. So these surfaces are self-cleaning. With PBS washing, bacteria that were on the surface but did not adhere to it, could easily be removed. No E-Coli bacteria can be seen in the microscopic image of the sample irradiated with 5000 number of pulses. So the adhesion force between the superhydrophobic surface and E-Coli bacteria is so low and bacteria can not adhere on the surface. In addition, if there is any bacteria on the surface, it can be removed easily by washing.

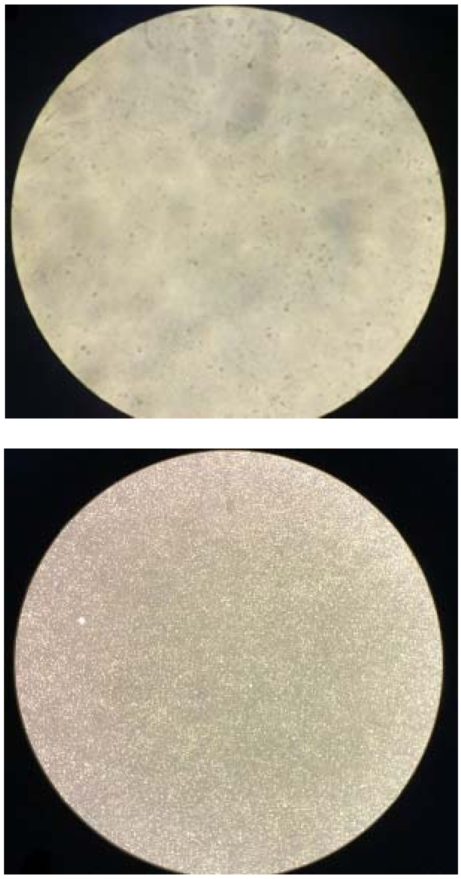

Fig. 4. Microscopic images of up untreated and down the sample irradiated at the fluence of 35 mJ/cm^2 with 5000 number of pulses. The microscopic images are one hundred times larger than the original.

3.3. Morphology

Fig. 5 shows the FESEM images of the irradiated sample with 5000 pulses, as a superhydrophobic specimen, with different magnifications. These images were taken after the bacteria culture to ensure that no bacteria is adhered to the superhydrophobic sample.

As it can be understood from the figure, micro-nano scale structures are formed on the surface following irradiation with 5000 pulses at fluence of 35 mJ/cm^2. Fig. 5 (a) shows the microstructures formation on the irradiated polycarbonate with 5000 pulses and (b) shows the nanostructures formation on the microstructures with higher magnification. As it can be seen from the image, nano spheres with diameter of about 60-90 nanometres are formed on the whole parts of the microstructures. This structure are similar to one was formed on the polymers following irradiation with an excimer laser at near the ablation threshold fluence [17, 18].

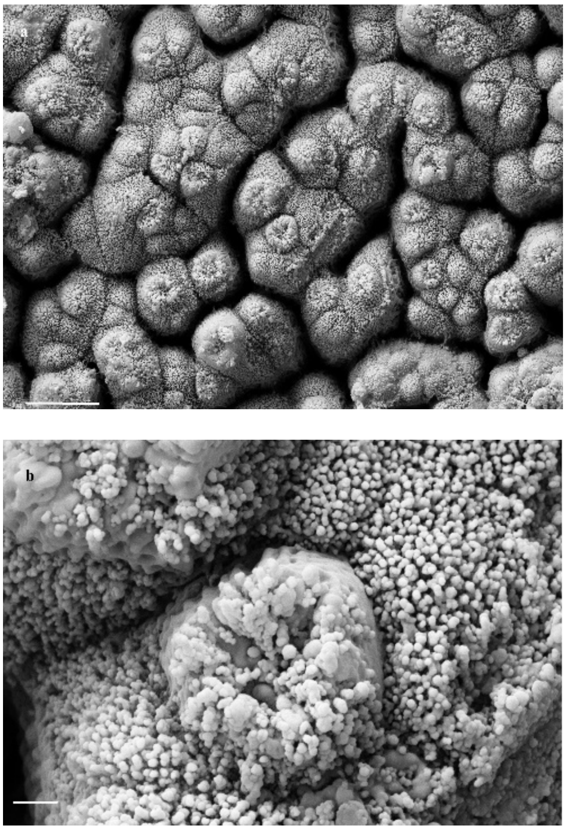

Fig.5. FESEM images of the sample irradiated at the fluence of 35 mJ/cm^2 with 5000 number of pulses after bacterial test at different magnification. Marked scale bar is about a) 4 micron, and b) 400 nm

4. Discussion

Laser irradiation of polymers at the ambient with nanosecond laser leads to different chemical and morphological changes based on the laser fluence regime. Material removal, morphological changes and micro scale structures formation are expected to occur at the fluences above the ablation threshold. In this case, the surface hydrophobicity is expected to increase. At the fluences below and close to the ablation threshold, chemical modifications and polar group's formation are occurred and these changes can turn the surface into the hydrophilic one, according to number of laser pulses. It is important to note that the number of laser pulses is the main factor in laser-matter interaction at the fluence below and close to the ablation threshold. At this fluence, chemical changes are occurred; but as it was mentioned, the intended fluence is so close to the ablation threshold and with high number of pulses, formation of nano size structures is expected [19].

Following irradiation of the sample with 1000 and 2000 number of pulses, chemical changes are occurred followed by polar group's formation as was mentioned in the previous paragraph. These polar groups may interact with H_2O molecule and cause surface to become hydrophilic.

With higher number of pulses as 5000 at this fluence, the energy of the laser pulses cause the creation of the structure and nano scale structures can be formed on the surface. 1000 and 2000 number of pulses are not enough for suitable nanostructures formation. Cassie-Baxter model predict that on the surfaces with micro/nano structures, air pockets can be entrapped in the structures and the surface shows superhydrophobicity behaviour [20].

Fig. 5 shows the hierarchical structures formation on the irradiated PC with 5000 number of pulses. Hierarchical structures formation on the surface is supposed to be one of the best approaches for artificial superhydrophobic surfaces fabrication [21]. In these surfaces, air is entrapped between the structures and the water droplet will be in contact with gas phase instead of the solid [22]. So the water contact angle of these surfaces will be so high and they have potential to be superhydrophobic surfaces. Air trapping in-between the fabricated structures is the main reason for their superhydrophobicity. Since no bacteria can be seen in these FESEM images, the superhydrophobic fabricated polycarbonate have antibacterial properties.

Both hydrophilic and superhydrophobic surfaces are used in many industries due to their vast applications. Hydrophilic surfaces can be used in biomedical, heat pipes and many other applications [23], while research has shown anti-biofouling, antibacterial and self-cleaning properties of superhydrophobic surfaces [24, 25]. So based on a specific application, the desired surface wettability can be obtained using a laser treatment method.

Numerous articles have reported that bacteria prefer to adhere to the solid phase rather than the gas [26, 27]. As was mentioned before, air trapping in the fabricated structures occurs. So bacteria will contact with the air as a gas phase instead of the surface as a solid phase. So bacterial adhesion on this surface will be at the lowest level and this surface is antibacterial one.

5. Conclusions

Due to the increasing bacterial resistance to antibiotics and the fact that the development of new strains of drug-resistant bacteria is expected to be faster than the production of new drugs in the next few years, the development of antibacterial surfaces that prevent the bacterium from initial adhesion to the surface has received much attention in the last decade. Superhydrophobic surfaces are reported to be the antibacterial ones. There are many approaches for superhydrophobic surfaces fabrication but laser treatment, as a simple and single-step method which can form suitable structures on the surface, is considered to be one of the best methods for this purpose. In this paper, effect of laser treatment of polycarbonate on its wettability and antibacterial properties was investigated. The polycarbonate samples were irradiated with an excimer laser at the ablation threshold fluence with different number of pulses. Chemical modifications such as surface carbonization and polar group's formation, as well as morphological changes including micro/nano structures formation are the reasons for wettability modifications of the irradiated samples. The number of pulses is the most important factor affect the wettability at the fluence below and near the ablation threshold. With 1000 and 2000 number of pulses, polar groups are formed on the surface which cause the surface become hydrophilic, while with 5000 number of pulses, nanostructures are formed on the irradiated surface and the surface is changed into the superhydrophobic one. Therefore, according to the experimental results, it is clear that the wettability in this fluence can be changed drastically with the number of laser pulses.

FESEM of the irradiated sample with 5000 pulses, shows the nanostructures formation on the surface. Air-trapping between these structures is the main reason for superhydrophobicity of this sample.

Bacterial adhesion test was done for the pristine and the superhydrophobic fabricated surface. After PBS washing, microscopic images of the surfaces were taken. According to the images, no adhered bacteria can be seen on the superhydrophobic surface, while many adhered bacteria are on the pristine polycarbonate. Bacteria prefer to adhere to the solid phase rather than the gas. Therefore, since there is air between the structures created on the superhydrophobic surface based on the Cassie-Baxter model, bacteria have little contact with the solid phase and most of the contact is with the gas phase. Therefore, this surface has antibacterial properties.

Finally, in this research, superhydrophobic antibacterial polycarbonate is fabricated using an excimer laser treatment. This fabricated sample can be used in many industries such as food, water and medicine.

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