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Surface modification of PMMA via UV and IR nanosecond laser treatment: similar morphological effects

Scientific research paper

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ABSTRACT

Surface engineering of polymeric materials is essential for improving their properties in various applications. In this study, we investigate the formation of similar morphological structures on the surface of polymethyl-methacrylate (PMMA) following irradiation of nanosecond ultraviolet (UV) and infrared (IR) lasers. Above the ablation threshold, and under certain irradiation condition, both UV and IR irradiation lead to formation of micro pores due to thermal stress and impurities. Again, irradiation of the samples first at a fluence above and then below the ablation threshold, with UV wavelength, leads to formation of bumpy structures compared to the nano spheres formed following IR irradiation. Our findings provide insights into laser-induced surface modifications in polymers and contribute to the development of controlled surface engineering techniques

1 Introduction

The field of surface engineering has witnessed significant advancements in various industrial and medical applications. Researchers in this field have explored diverse methods of surface processing and material property modification, such as antibacterial treatments and enhancement of surface hydrophilicity. Among the various chemical and physical methods employed for surface modification, laser processing techniques have gained considerable popularity due to their high speed, simplicity, flexibility, accuracy, and cost-effectiveness, especially in industrial-scale applications [1, 2]. During the last 30 years, modification of morphological and optical properties of various materials by fabrication of micro/nano patterning on their surface has been widely investigated for use in modern devices such as optical ones [3-7]. Surface morphology plays a crucial role in determining surface properties and has a significant impact on the physical characteristics of a material's surface, such as hydrophilicity, heat transfer in microchips, and bacterial adhesion [8-10]. Following laser irradiation under specific irradiation conditions, different structures, in dimensions and density, are formed on the surface of polymers. The type and extent of the modification depend on the irradiation conditions. Modifying the physical and optical properties of polymers, such as wettability, biocompatibility, refractive index and light absorption, are among the applications of these structures, which are used in the manufacture of various tools, including the optical devices. Therefore, investigating and understanding the micro/nano-structural changes induced by different surface modification methods is of great importance while considerable number of studies have been conducted on the effect of laser irradiation parameters on the surface properties of polymers [4, 11-14].

Polymethyl-methacrylate (PMMA), known for its exceptional properties including biocompatibility, flexibility, and cost-effectiveness, has emerged as a popular material in surface engineering for microfluidic device fabrication [1]. Chemical and wettability modifications of the PMMA have been investigated with various lasers, including Nd:YAG,

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HPDL, excimer and CO_2 lasers [15]. In this research, the formation of similar micro/nano structures (morphological aspect) on the surface of PMMA under laser irradiation at two different laser wavelengths (ultraviolet (248 nm) and infrared (9.55 microns)) is studied. The effect of the laser irradiation parameters on the morphological changes was examined.

2 Experimental

2 mm thick polymethyl-methacrylate sheets with 10×10 mm^2 dimensions were used as the sample material. Prior to irradiation, all the samples were cleaned in methanol using an ultrasonic bath. A pulsed CO_2 laser with a pulse duration of 100 ns and a wavelength of 9.55 microns, and a nanosecond KrF laser with a wavelength of 248 nm and a pulse duration of 25 ns were employed as the radiation sources. Spherical lens with focal length of 100 cm and 20 cm were used for the irradiation with CO_2 and KrF lasers, respectively. The laser fluence was controlled with changing the sample distance from the lens. The formed structures on the surface were examined using scanning electron microscopy (SEM VEGA3- TESCAN company).

3 Results and Discussion

As it was mentioned in the introduction, laser-induced surface structures are observed on various materials after irradiation under a wide range of conditions. These structures have the ability to control the optical, mechanical, thermodynamic, and electrical properties of the sample surfaces. Furthermore, they can influence the surface wettability. However, the mechanisms underlying the formation of these structures upon laser irradiation remain a subject of ongoing researches. Different morphological changes happen on the samples regarding the laser irradiation fluence, above and below the ablation threshold. The fluence for the laser ablation threshold of PMMA is approximately 200 mJ/cm2 and 1500 mJ/cm2 at 248 nm, and 9.55 microns, respectively [1, 16]. For the investigation of the effect of the irradiation parameters on the morphological changes, samples were irradiated at 2 fluence regimes of the irradiation: above and below the ablation threshold, for each wavelength, with different number of pulses and fluences.

3.1. The fluences above the ablation threshold

Figure 1 a shows SEM image of the PMMA sample before irradiation. A nearly smooth surface without any discernible roughness is observed before laser irradiation. However, SEM images of the polymer surface after irradiation above the ablation threshold at both UV and IR wavelengths (Fig. 1b and 1c, respectively) reveal the formation of micro pores.

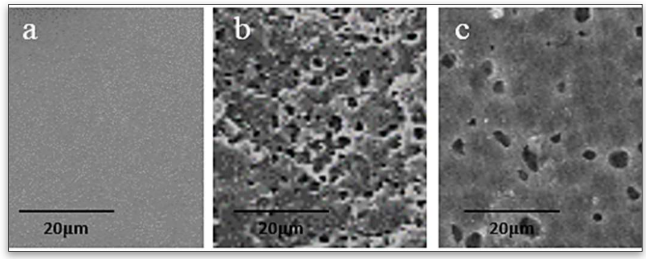

Figure 1. Scanning electron microscopy (SEM) images depicting the surface characteristics of PMMA: a) Pristine PMMA surface, b) Surface morphology of PMMA after UV irradiation (fluence=800 mJ/cm^2, and pulse number=1), and c) Surface morphology of PMMA after IR irradiation (fluence=2000 mJ/cm^2, and pulse number=1).

The formation of surface pores on polymers following laser irradiation has been observed in previous studies [17, 18]. Similar pore-like structures have also been observed on glass surfaces after infrared laser irradiation and on copper plates irradiated by femtosecond lasers [19-21]. However, the exact mechanism behind their formation remains not fully understood. It appears that the rapid generation of large temperature gradients, leading to thermal stress, is a significant factor in creating these micro-pores using nanosecond laser irradiation, regardless of the laser wavelength [22, 23]. At a sufficiently high stress, the rearrangement of the defective crystal structure and inelastic effects lead to release of residual strain during solid deformation. Therefore, localization of the stress relaxation through the formation of the relaxation zones associated with the collective behavior of the excited atoms by laser beam cause deformation. The relaxation zones can be assigned to dislocations, clusters, and the groups of vacancies, forming the dislocation loops, micro-pores, micro-cracks, etc [24]. Additionally, at high fluence of laser, specially using CO_2 laser that has high thermal effects, the flow dynamics of melt pool created by laser irradiation, predominantly results in micro-structuring. Melting layer may lead to the formation of the spatial non-homogeneity on the irradiated area. Because of this non-homogeneity, ejected material from areas on the melt layer may produce micro-holes [1].

Other possible mechanisms, such as rapid self-quenching, decomposition of specific components, depolymerization of the polymer matrix, and evaporation of solvents within the bulk of the polymer and bubble bursting, have also been proposed to explain the appearance of the porous microstructures on polymers following laser irradiation [16].

As shown in Figs. 2 and 3, the density of micro-pores increases with increasing the laser fluence at both laser irradiation wavelengths. The same behavior is observed with increasing the number of pulses (Figs. 4 and 5). In fact, the impurities inside the polymer, which cannot be ablated from the surface at lower laser fluence or number of pulses, are ablated from the surface at higher fluences or more pulses, which leave cavities behind [16].

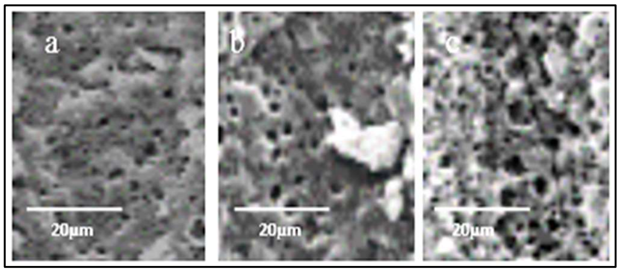

Figure 2. SEM images showing the surface morphology of PMMA after KrF laser irradiation above the ablation threshold with 50 pulses at different fluences: a) 400 mJ/cm^2, b) 500 mJ/cm^2, and c) 800 mJ/cm^2.

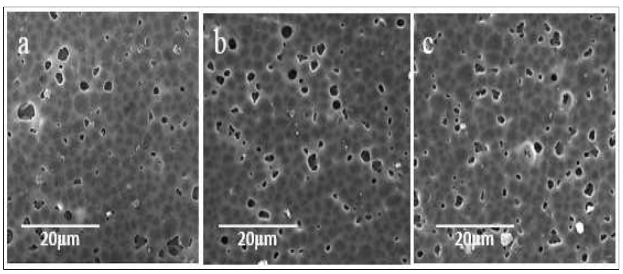

Figure 3. SEM images illustrating the surface morphology of PMMA after CO_2 laser irradiation above the ablation threshold with 50 pulses at different fluences: a) 5000 mJ/cm^2, b) 10000 mJ/cm^2, and c) 20000 mJ/cm^2.

As it is clear in Figs. 2 to 5, with increasing the laser fluence and the number of pulses, the size of the pores also increases. The reason for this is that increasing the number of shots and fluence makes the thermal effects more noticeable. As a result, the more intense temperature rise, the faster the gaseous products explode blowing away some of the surrounding substrate [25]. In addition to that, with increasing the fluence, the possibility of releasing more stresses at the same time makes the dimensions of the holes larger [1].

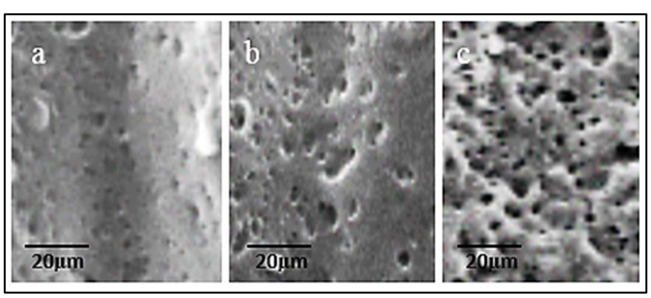

Figure 4. SEM images displaying the surface morphology of PMMA after KrF laser irradiation above the ablation threshold at a fluence of 800 mJ/cm^2 with different pulse numbers: a) 50, b) 100, and c) 150.

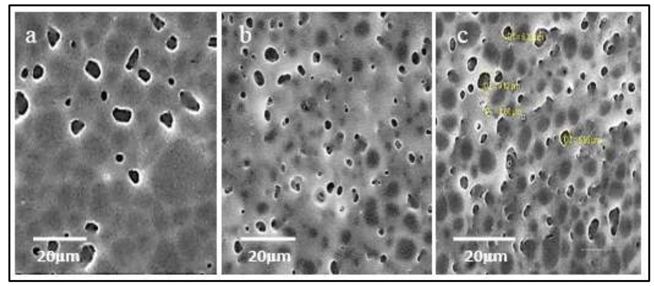

Figure 5. SEM images demonstrating the surface morphology of PMMA after CO_2 laser irradiation above the ablation threshold at a fluence of 2000 mJ/cm^2 with different pulse numbers: a) 50, b) 100, and c) 150 [1].

3.2. Fluences below the ablation threshold

At fluences lower than the ablation threshold, no significant changes were observed in the morphology of the polymer surface irradiated with the CO_2 laser with a pulse number less than 3000. However, with increasing the number of pulses to 3500 pulses, nano-spheres appear on the surface (Fig. 6). On the other hand, irradiation of the sample with 50 pulses of KrF laser at a fluence of 400 mJ/cm^2, followed by 10000 pulses at the fluence of 20 mJ/cm^2, results in nano bumpy structures (Fig.6).

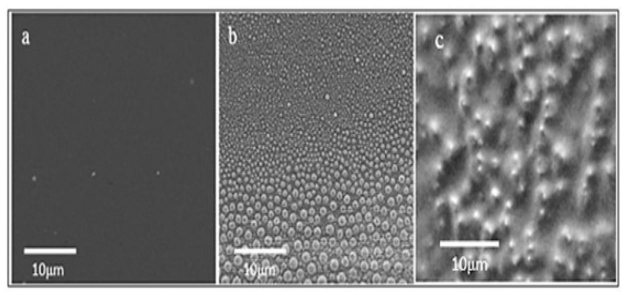

Figure 6. SEM images showing the surface morphology of PMMA after: a) CO_2 laser irradiation below the ablation threshold at a fluence of 500 mJ/cm^2 with 2000 pulses, b) CO_2 laser irradiation below the ablation threshold at a fluence of 500 mJ/cm^2 with 3500 pulses [1], and c) KrF laser irradiation below the ablation threshold at a fluence of 20 mJ/cm^2 with 10000 pulses**.**

The possible mechanisms for the formation of spherical and bumpy structures on the PMMA surface following laser irradiation with a high number of pulses at fluences below the ablation threshold have been proposed as follows:

- Due to the chemical structure changes of the polymer, with increasing number of pulses, incubation effect occurs. As a result, the fluence of the ablation threshold of the irradiated area on polymer decreases. The formation of spherical structures at a threshold number of pulses shows that they may be the same as the conical structures. Then the basic mechanism for their formation can be explained by the models used to describe conical structures [1].

Various models have been proposed to explain the formation of cones on polymers due to laser irradiation, however, the formation of conical structures is mainly described by shielding the laser beam from different areas of the material with different percentages of impurities or the accumulation of debris between pulses. [11].

Additionally, material properties such as the absorption at the laser wavelength, the thermal and mechanical properties as well as irradiation parameters play a key role in the shape and the size of these structures [15].

• Creation of humps due to crystal-amorphous phase transition, melting or plastic flow is another possible mechanism in the formation of these structures, which is called "Laser swelling" [26]. In fact, the temperature of the material due to laser pulse irradiation can reach higher than the melting or boiling point of the material and create a metastable liquid state. In this case, if the temperature of the substance reaches the thermodynamic critical point, the superheated liquid turns into droplets where fast freezing of these bubbles after the termination of laser pulse can create spherical structures [27].

Again, study of the bumpy structures created on the surface of SiGe after KrF laser irradiation [28], shows that the scattering of laser light caused by porosity or surface defects is one of the reasons for creating these structures. The rate of emergence of these structures during IR irradiation is higher compared with the UV irradiation. This difference can be attributed to the higher optical absorption of the polymer in the UV region, which reduces the thermal effects and the formation of the thermal structures on the surface.

4 Conclusions

Surface engineering of polymer materials plays a crucial role in their utilization as substrates in various applications, including biology and micro-electronics. The manipulation of surface microstructures greatly impacts the properties of these materials. Nanosecond laser irradiation offers a cost-effective and precise method for creating micro- and nano structures on polymer surfaces. The findings of this study indicate that similar micro/nano structures can be formed on the surface of polymer following IR and UV laser irradiations with controlling the irradiation parameters. Overall, nanosecond laser irradiation provides an effective approach for tailoring the surface properties of polymer materials, offering potential applications in various fields requiring precise control over surface microstructures. Further investigations and optimizations lead to enhanced surface engineering techniques and expanded applications of polymer materials.

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