



The influence of pulsed CO₂ laser irradiation on the optical properties of PMMA

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ABSTRACT

In this paper, effect of the pulsed CO₂ laser irradiation on optical properties and surface morphology of PMMA was investigated. The samples were irradiated by a CO₂ pulsed laser with the wavelength of 9.55 micron and the pulse duration of about 100 ns. UV-Visible spectroscopy and Scanning Electron Microscopy (SEM) were used for investigating the change in absorption, reflection, refractive index and surface morphology, respectively.

Keywords: Pulsed CO₂ laser, PMMA, Optical properties, Morphology

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INTRODUCTION

Optical properties modification of polymers has been extensively investigated for achievement of desired properties for using in modern optical devices, such as polymeric waveguide technologies (Eldada & Shacklette, 2000). Optical properties of polymer are dependent on the specific polymer, the formulation of polymer and crystallinity. However, chemical or mechanical degradation or even temperature treatment can change the optical properties of polymers and influence their formulation. Depending on initial photon energy, photons will couple into the available vibrational or electronic states. For example, in insulators or semiconductors the absorption of light usually occurs through resonant

excitation such as transition of valance bond to the conduction bond or within bonds (Baeuerle, 2000). Energy can be transferred from excited bonds to lattice phonons. If the energy of a photon is lower than the energy gap, it can't be absorbed. Nevertheless defects, multiphoton absorption and impurities may cause absorption (Baeuerle, 2000).

Laser irradiation is used as a standard method for surface modification and optical properties changes in different materials especially polymers. Following irradiation different chemical, optical and morphological alterations occur dependent on the irradiation parameters like the laser wavelength, the fluence, the pulse number, pulse repetition rate and the pulse duration. The most important parameter affects laser-material interaction at a given wavelength is the



laser fluence. At high fluences, large temperature gradient and small localized laser heating can lead to rapid self-quenching (Kim, Park, & Hong, 2007) of the material. Thermal stress can be induced by the rapid generation of large temperature gradients (Wang & Xu, 2001). These stresses can lead to cracking, surface morphology modification or optical properties changing. On the other hand, radical formation and nanostructuring of the surface are two important results of laser irradiation at fluences below the ablation threshold. Poly (methyl methacrylate) (PMMA) is one of the polymeric materials which is of interest because of its attractive properties. It is inexpensive, biocompatible, and thus ideal for disposable devices in clinical, biological, and chemical applications (Scully, Baum, Liu, & Perrie, 2012; Spasojevic et al., 2015; Zahedi & Dorrnian, 2013). Again, its appropriate absorption at CO₂ laser wavelength facilitates its use in CO₂ laser micromachining for manufacturing microfluidic and optofluidic devices. In this research, optical properties modification and surface morphological changes of PMMA following pulsed CO₂ laser irradiation are investigated.

EXPERIMENTAL WORK

Poly (methyl methacrylate) was cut in to pieces with a thickness of 1mm. Samples were irradiated by pulsed CO₂ laser with 100 ns pulse duration and 9.55 μm wavelength at different fluences and with various number of pulses. Optical absorption and transmission spectra of pristine and irradiated PMMA were recorded in transmission mode with a step size of 2 nm, in the wavelength range of 400 to 900 nm using a UV-visible spectrometer (UV 2100, Border Company) at room temperature. Surface morphology was investigated by scanning electron microscopy (SEM). The reflection (R) and the refractive index (n) were calculated by using the following equations (Al-kadhemy, Saeed, Kadhum, Mazloun, & Aied, 2014; Zahedi & Dorrnian, 2013).

$$A + R + T = 1 \quad (1)$$

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (2)$$

Where, A is the absorbance, T is the transmittance and k is the extinction coefficient (Calloway, 1997),

$$k = \frac{\lambda\alpha}{4\pi} \quad \alpha = 2.303 \frac{A}{\text{Thickness}} \quad (3)$$

$$\text{Because } k^2 \ll \frac{4R}{(1-R)^2}$$

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2}} \quad (4)$$

RESULTS AND DISCUSSIONS

The fluence for the single pulse ablation threshold of PMMA samples was obtained experimentally to be about 1.5 J/cm². Then samples were irradiated with different number of pulses at fluences above and below the ablation threshold. Fig.1 a, b shows the change in transmission, reflectance and refractive index of the samples irradiated at the fluence of 0.5 J/cm² with different number of pulses and Fig.2 and 3 show the results for samples irradiated at the fluence of 10, 30 and 50 J/cm². As it can be seen from the figures, for all the samples and with increasing the number of pulses, the surface transmission decreases; while, the changes in reflection and the refractive index are dependent on the laser fluence and the number of pulses. The changes in the refractive index and the reflectance are the same; Both reflection and refractive index increase with increasing the number of pulses at the fluence of 0.5 J/cm², while they increase first at the fluence of 10 and 30 J/cm² and then decrease. Both R and n increase continuously at the fluence of 50 mJ/cm² with number of irradiated pulses used in this experiment. Following laser irradiation, different mechanisms may lead to modification of optical properties like transmittance, reflectance and refractive index. These are including production of radicals, bond breaking due to laser irradiation, melting and morphology changing. The changes in surface morphology is very important parameter affect the surface properties. The changes in surface morphology is a result of laser irradiation with high number of pulses at fluences below the ablation threshold or lower number of pulses at fluences above the ablation threshold.

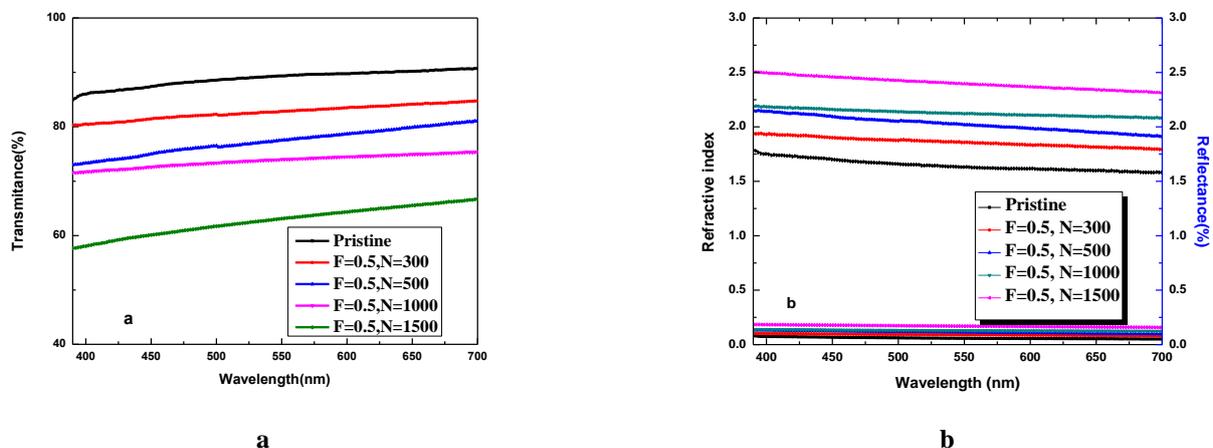


Fig.1 a) Transmission and **b)** Reflectance and refractive index at the fluence of 0.5 J/cm² with different number of pulses

The investigation of the surface morphology of irradiated PMMA at the fluence of 0.5 J/cm² shows that no change in surface morphology is seen following irradiation with different number of pulses up to 3000. Then, other mechanisms should be account for the change in the spectrum intensity following irradiation at the mentioned parameters. Results of different experiments shows that laser irradiation of polymers at fluences below the ablation threshold leads to formation of different radicals on the surface (Jelvani, Pazokian, & Farisar, 2013; Pazokian, Barzin, Mollabashi,

Jelvani, & Abolhosseini, 2012; Pazokian, Jelvani, Mollabashi, Barzin, & Farahani, 2011). The radical or new bond formation is also caused UV-Vis spectrum intensity changes (Rai, Mukherjee, & Jain, 2016). The changes in spectrum will be saturated due to decreasing the number of radicals when laser irradiation continues. For example, elimination of C=O and O-H bonds may cause new bond formation between H₂O in air and oxygen atom in PMMA. Higher number of pulses can induce higher sample temperatures and it may result in the elimination of C=O and O-H bonds.

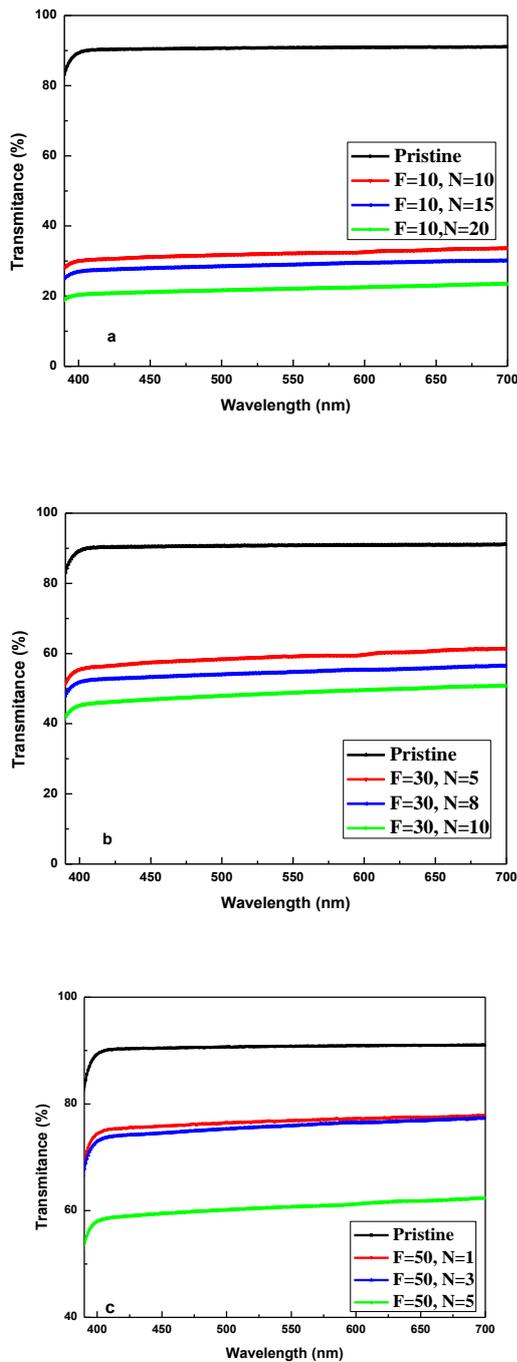


Fig.2 Transmittance spectra of the samples irradiated at the fluence of , a-10, b-30 and c-50 J/cm².

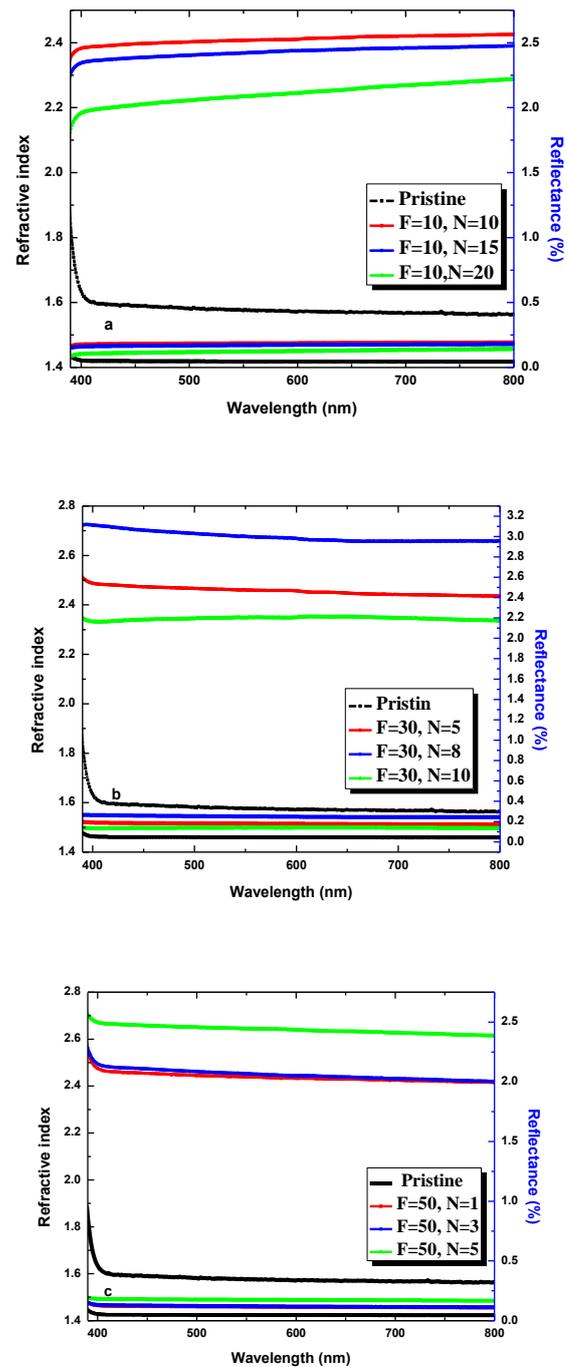


Fig.3 Refractive index and reflectance of the samples irradiated at the fluence of , a-10, b-30 and c-50 J/cm².

Again, the formation of microstructures at fluences above the ablation threshold has significant effect on surface properties. Fig.4 shows typical scanning electron microscope images of

the surface irradiated with 5 pulses at the fluence of about 10 mJ/cm²

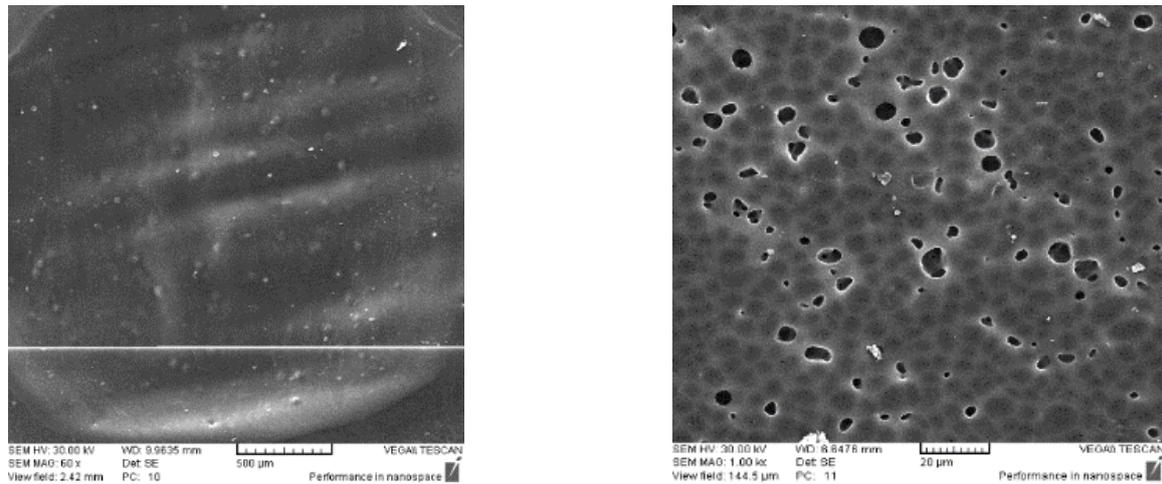


Fig.4 Scanning electron microscope images of the surface irradiated with 5 pulses at the fluence of about 10 mJ/cm² with different magnifications

Micro pores are formed on the surface of PMMA following irradiation at the fluences above the ablation threshold. Micro pores are formed on the surface of PMMA following irradiation at the fluences above the ablation threshold. The light trapping and in the pores and it's scattering from their edges may lead to change in the absorption and reflection intensity in the spectra. However, the effect of the pore formation on the spectrum depends on their number density and size which are dependent on the laser fluence and number of pulses. Increasing the size and the number density of the pores at the fluence of 50 J/cm² (is not shown) may be a reason for different behavior of the reflection and refractive index spectra at the fluence of the 50 mJ/cm² versus the other two fluences. On the other hand, the ablation is saturated with lower number of pulses at higher fluences. Nevertheless, different reasons may affect the optical properties changing which needs further investigations. Cross-linking following irradiation, new bonds formation or oxidation, crystallization, molecular weight changing, self-quenching, thermal stresses, multi-photon absorption and nonlinear optical effects at high fluences, small produced cracks, defects, microstructures and surface morphology changing are some of the reasons for optical properties modification. On the other hand, for polymers irradiated at IR or NIR, a photothermal

mechanism is found. In this case, four classes of mechanisms may appear: random chain scission, end-chain scission, chain-stripping, and cross-linking (Kappes, 2012). Generally, if the temperature of polymer is more than glass transition (T_g), devitrification will occur (Pazokian et al., 2012), causing increasing density (Qi et al., 2013). A change in density leads to refractive index modification.

CONCLUSION

PMMA polymer was irradiated with a pulsed CO₂ laser to investigate the effect of the laser irradiation on its optical properties. The results of the experiments show that the absorption increases for all the sample irradiated at fluences below and above the ablation threshold. However, the changes in reflection and refractive index depend on the laser fluence. The formation of different radicals on the surface following irradiation below the ablation threshold and a change in surface morphology upon irradiation above the ablation threshold are supposed to be the most important factors affect the optical properties changes. However, the other reasons were suggested for the explanation of the modification of the spectrum intensity, which need further investigations.

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