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Hydrophobic Investigation of Excimer Laser Effects on Poly (Ethylene Terephthalate)

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ABSTRACT

The modification on the surface of the polyethylene terephthalate (PET) polymer as a result of ArF (193nm) laser irradiation was investigated. Fourier transform infrared spectroscopy (FTIR) and energy-dispersive X-ray (EDX) spectroscopy were employed for examination of the chemical composition of irradiated surface and conical structure. FTIR spectroscopy indicates that by irradiation of PET, hydrophobic groups of the polymer molecules in the polymer chain have more freedom of movement and prevents from the interaction between water molecules and the hydrophilic groups on the polymer surface, and PET surfaces after exposure have become more hydrophobic. While the PET is irradiated by more than 800 pulses, its surfacs become hydrophilic, so that the surface of PET after treated by 1500 pulses, even become more hydrophilic than that of untreated one.

Keywords: ArF laser, Hydrophobic, Laser ablation, Poly ethylene terephthalate

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INTRODUCTION

Research and development in excimer laser polymer ablation has been actively pursued for some twenty years, driven by interest in the basic science as well as by numerous applications that have emerged for this high-resolution technique for material removal (Krüger, Niino, & Yabe, 2002). For technical applications as well as the fundamental understanding of the ablation behavior, the determination of ablation threshold fluence as well as etch rate is of interest (Srinivasan, 1994). The interaction of laser light with matter causes permanent changes in the material properties that cannot be achieved easily with other methods (Dyer, 2003). Now the laser light use to irradiation of polymer surfaces due to lack of adverse effects on polymers. It is now more than thirty years since publication first appeared on using UV excimer lasers to process polymers in the form of conventional resist and as self-developing resist. Characteristics of hydrophilic and hydrophobic of polymeric surfaces after laser irradiation show different behaviors depending on the type of used polymer and the conditions of laser irradiation such as fluence, pulse width and pulse repetition frequency, as well as due to changes in the morphology and bonds of surface are interpreted (Jaleh, Parvin, Sheikh, Zamanipour, & Sajad, 2007; Parvin et al., 2014; Qi, Chen, Yao, & Zuo, 2008).

Self-assembled, close-packed cones occurred in PET, in which heat generated due to absorbed laser energy creates a thin, chemically stable, viscoelastic, highly compliant layer. Surface structure in such polymers evolves from nodules through donuts into ripples and finally to cones as the energy deposited per unit area on the surface is increased using a combination of single pulse fluence and number of pulses. A phase transition from a ripple phase to a cone phase is thought to occur as the thickness of the viscoelastic surface layer increases above a critical value (Murthy, Prabhu, Martin, Zhou, & Headrick, 2006). Finally, UV laser modification process is essentially a dry process, which dose not involve

any solvents unlike the wet chemical process, and the thus eliminates environmental pollution.

In this work, the modification of PET surface after ArF laser irradiation was investigated. The FTIR and EDX spectroscopy were employed for examination of the chemical composition of irradiated surface and dependency of hydrophilic and hydrophobic characteristics on number of pulses.

EXPERIMENTAL PROCEDURE

Commercially available PET films were used for the study of laser irradiation on polymer. UV treatment of PET samples was performed by a pulsed UV excimer laser (Lambda Physik LPX 220i) under standard atmospheric conditions. The laser operated with ArF gas and produces a wavelength of 193-nm. The applied fluence was 100 mJ/cm^2 (above the ablation threshold) and the number of pulses was varied. The pulse repetition rate was kept constant at 1Hz to avoid heat accumulation. Energy reaching samples was measured by a Joulmeter (Molectron JD2000) prior to irradiation. PET samples were submitted to laser radiation at normal incidence in atmospheric conditions. Prior to laser exposure, the samples were ultrasonically cleaned for 5 minutes, in a bath containing 10% acetone and water, and then dried in air. Laser fluence range, below and above the fluence thresholds and different pulses number were used. SEM investigations of the laser treated PET samples were performed with a QUANTA 200 instrument. To check the hydrophilic or hydrophobic of the surface after irradiation of samples was taken FTIR spectrum.

FTIR and EDX measurements were recorded on a digital model MIR TGS spectrometer with the resolution of 4 cm^{-1} and within the scan range of 4000-830 cm^{-1}. Static contact angles were measured using the sessile drop method with contact angle measurement equipment.

RESULTS AND DISCUSSION

Modifications of PET surface after laser irradiation were investigated in order to determine their nature as well as their evolution with process parameters. The laser beam fluence is also a key to predicting ablation behavior in polymeric structures while fluences below the critical threshold fluence may be effective in modifying surface chemistry and even morphology, for material removal and true ablation to occur, the threshold fluence must be reached. The figure 1 shows a progressive change in the morphology versus fluence from an unexposed area to an ablated surface, and then onto an area of densely packed cones that give way to an area in which the cones are widely separated in the middle of the exposed area where the fluence is the highest. The surfaces in figures 1b, 1c and 1d were further explored by irradiating a sample at lower total fluences (5-20 mJ/cm^2). After exposure at an energy density below the ablation threshold, microscopy observation dose not show any ablation and cone structure formation. Figure 1e shows the surface features near the middle of another sample irradiated at 50 mJ/cm^2. A close-packed conical structure is seen in the transition region (Fig1f). In polymer ablation literature, the results from different polymers are often explained using similar mechanisms. Interference between incident and the scattered parts of the laser beam and the laser beam shielding by the re-deposited ablation debris and possible impurities, can create conical structure (Wefers & Schollmeyer, 1993). It appears that the main reasons to explain the creation of conical structures based on the presence of impurities and carbonization of the surface. In this context and for evaluation the atomic composition of the obtained cones and compare those to the untreated surface, EDX spectroscopy have been utilized.

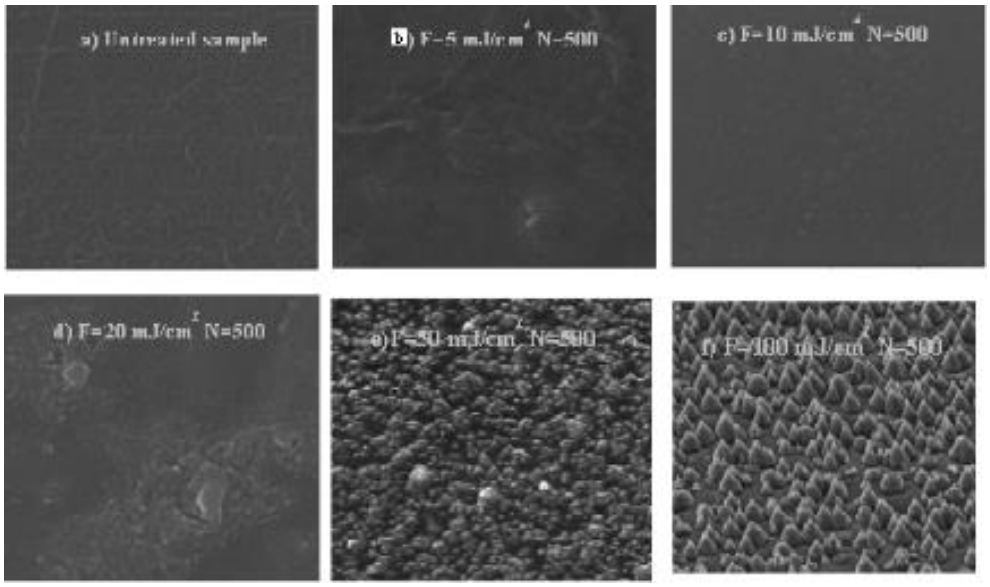

Fig 1. SEM of ablated area in PET polymer with constant number of pulses (N=500) and different fluences a) Untreated sample, b) 5mJ/cm^2, c) 10mJ/cm^2, d) 20mJ/cm^2, e) 50 mJ/cm^2 and f) 100 mJ/cm^2.

To do this, the abundance of carbon and oxygen were measured in different parts of cones. Fig 2 displays the created EDX spectra of cones on PET polymers. It is find from the EDX spectrum of polymer, in addition to carbon, oxygen and hydrogen in PET with $(C_{10}H_8O_4)_n$ chemical formula there are impurities such as Na, Au, S and Cl which likely impurities entered into the polymer created the cone-shaped structures.

It should be mentioned that one the main reasons for conical structures on the surface of PET is the removal of material and accumulating of them on the surface of polymer. In fact, in the case of nanosecond pulses, analysis of nanometer and micrometer sized polymer particles and their return to the surface causing the conical structures. The number of cones increases with the number of pulse and their height increases by increasing of the fluence.

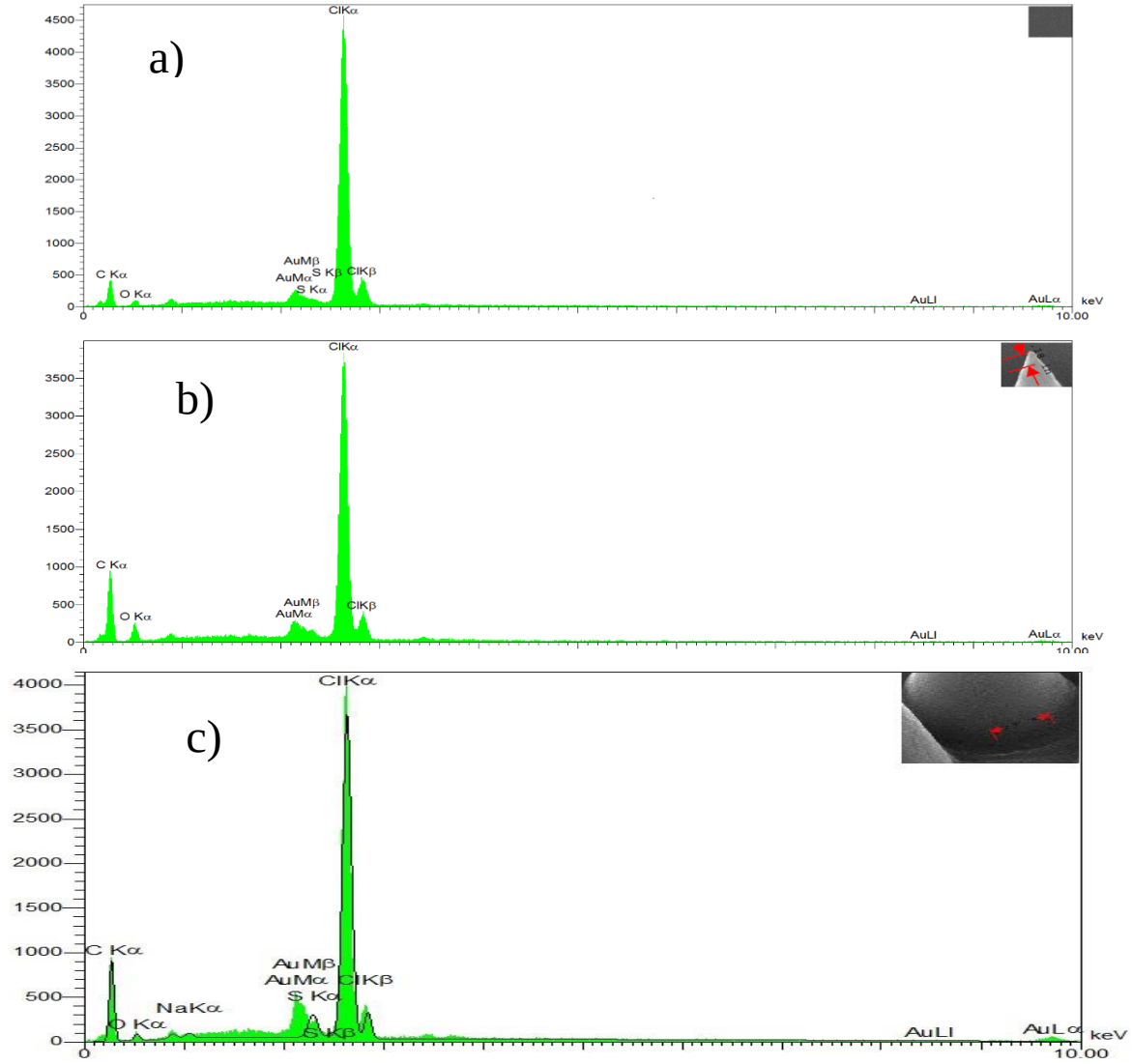

Fig 2. The EDX spectrum from different parts of cones created on PET at the fluence of 100 mJ/cm^2 and 500 pulses. a) Untreated sample, b) the apex of the cone and c) the basis of cone.

In addition chemical effects occur on the PET surface during excimer laser ablation; there is an agreement on the development of texture during ablation. By ablation, a regular, textured surface is formed with feature sizes in the order of microns. The developed surface structures are described as "rolls" or cones, and are depended on laser fluence as well as pulse dependent, with the structures becoming more prominent with additional radiation. These surface structures were observed with SEM images (Dadsetan, Mirzadeh, Sharifi - Sanjani, & Daliri, 2001). The transmition of the surface of PET has been investigated through the FTIR spectrum of samples

exposure with 250 and 1500 pulses and fluence of 50 mJ/cm^2 is shown in Fig3. In all samples that were performed the spectrum of them, the peaks of functional groups of the compound of PET are clearly showed.

Observed peak in 2900 cm^{-1} and 2800 cm^{-1}, related to the asymmetric and symmetric stretching vibration of -CH_2-, respectively. Since none of the recorded peaks before and after laser irradiation has been observed the functional groups of water (The stretching vibration peaks of OH in the 3400 cm^{-1}and the bending vibration peaks of OH in the1600-1650 cm^{-1}) have not observed that can be a cause of the lack of water absorption on the surface of the polymer and make it more hydrophobic

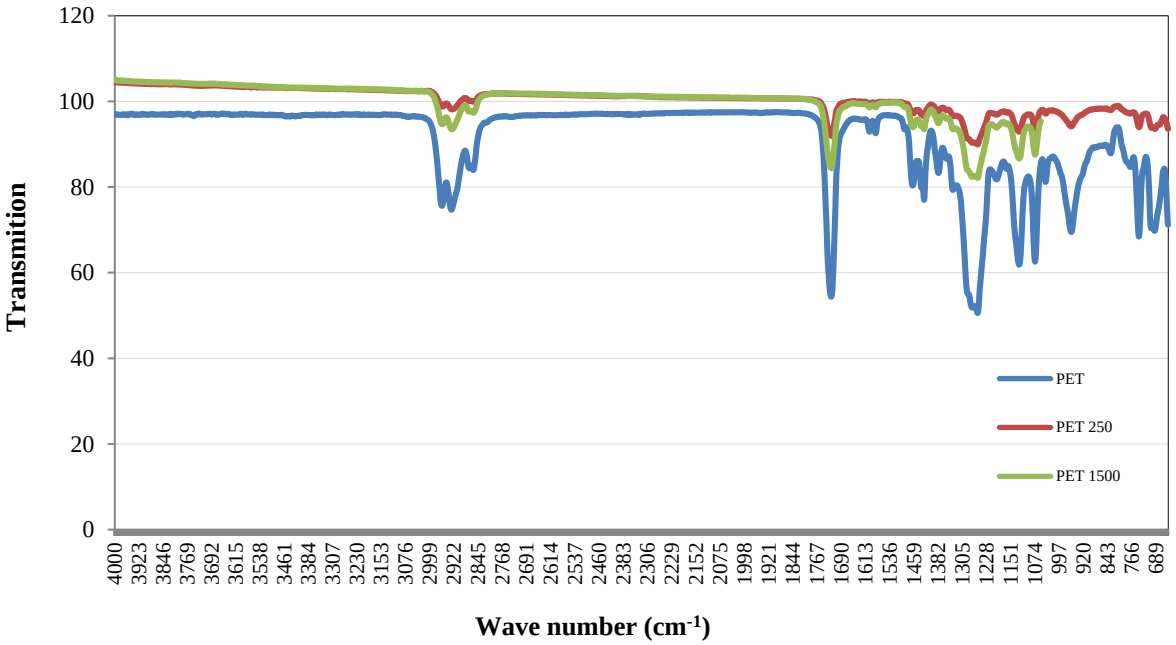

Fig 3. FTIR spectrum of untreated and irradiation sample of a PET polymer at 50 mJ/cm2 with 250 and 1500 pulses.

Contact angle measurements were performed in this study that showed a correlation between hydrophobic and the number of pulses in PET. For further investigation, the plot of contact angle of water versus the number of laser pulses for PET polymer at the fluence of 50 mJ/cm2 is given in Fig4.

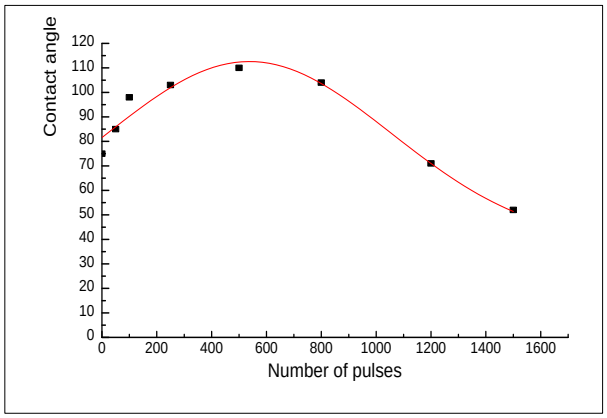

Fig 4. The contact angle of water versus the number of laser pulses for PET polymer at the fluence of 50 mJ/cm2.

As seen in Fig4, by increasing the number of laser pulses, the contact angle of surface has been increased, at first. The surface of the sample by radiation at 50 mJ/cm2 ablated and became rough and uneven and conical microstructures are made on the surface. It has been shown that one of the causes of surface hydrophobic can be related to the formation of cones (Jooybari, Afarideh, Lamehi-Racti, & Ghergherehchi, 2015). But, the contact angle after more than 800 pulses has been decreased, so that, in the 1500 treated pulses, the contact angle is lower than that of the others number of pulses, even than that of untreated sample. It is shown that for sample treated by 1500 pulse, the hydrophobic of surface has been reduced and become more hydrophilic.

CONCLUSION

The EDX spectra measurements indicate that the entered impurities into the polymer in the process of emergence of the cones have contributed. In addition to the significant changes in the morphology of the surface, changes in the hydrophobic arises from the modification in chemistry of the surface that depends on the photon energy and the number of laser pulses.

By analyzing the FTIR spectrum of samples after irradiation with ArF laser, it is finding that the surface become more hydrophobic.

The contact angle of water is depended on number pulses, so that, for number of below 800 pulses, the surface of PET become hydrophobic, while for more than that of, the PET become hydrophilic.

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