Cone evolution on ArF laser ablated 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. Scanning electron microscopy (SEM), was employed for examination of the morphology of irradiated surface and conical structure. The fluence and number of pulses for the formation of the structures were very important and determined the desirable or unwanted effects of the laser irradiation on the surfaces regarding the desired applications. The height of the cones was increased by the fluence while their numbers were reduced. The average of the apex angles of cones and the ablation threshold were determined.

Key Words: ArF laser, Cone structure, Laser ablation, Polyethylene terephthalate.

1. INTRODUCTION

Excimer laser ablation of highly absorbing polymers has been the subject of a large number of investigations during the last two decades. 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 [1]. The interaction of laser light with matter causes permanent changes in the material properties that cannot be achieved easily with other methods [2]. Now the laser light use to irradiation of laser 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 by laser pulses is one of the most active branches in this field [3-6].

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Due to unique features of polymers such as light weight, low cost, mechanical stability, good transparency, and high durability, they have been used at different technologies. And by modifying some features of polymeric materials with laser can be achieved the wider applications of polymeric materials. Modifying of surface structures and changes in the characteristics of biocompatibility of biocompatible polymers by laser pulses is one of the most active branches in this field [6-8]. According to studies in the field of optimized polymer films with laser has been specified that regular structure is created in the irradiated areas and improve the biocompatibility of polymer [9]. One of the important parameters of laser surface modification is laser fluence. During irradiation the surface with laser beam, according to fluence of the radiation, different phenomena can be occurred [10]. PET was modified by a KrF 248-nm excimer laser with high and low fluence. The PET surface develops usually a periodic roughness or ripples with high fluence. The roughness size was in the micron range and the surface shows signs of global melting [11]. In the polymers, some well oriented structures of hills and grooves or ripple structures in the range of micron have been developed on surfaces with irradiation fluence above the so-called ablation threshold. The threshold values are depended on the wavelength of the UV irradiation and the absorption coefficient of the polymer. The effects on chemical and physical properties of biaxial stretched PET as a result of KrF (248-nm) and XeCl (308-nm) laser irradiation were investigated. Below ablation threshold, roughening of the surface was detected, with the formation of periodic surface structures for 308-nm irradiation, while above the ablation threshold, dendrites or granular protuberances superimpose the densely-packed nap structures [12]. Polycarbonate and polylallyl di-glycol carbonate (CR-39) polymer were processed with ArF laser. Conical microstructures formed on laser-ablated CR-39. It was shown that cone shape walls were sharp tips together with interference and well defined fringe-structure around cone base. So, it was indicated that cone having different chemical structures compared to surface of CR-39 polymer [13]. So, the conical microstructures were formed on CR-39 ablated using 157-nm F2 laser radiation. These were distinguished by having smooth, straight walls and, for CR-39, sharp tips, together with interference and diffraction fringes around their base [14]. Finally, UV laser modification process is essentially a dry process, which does not involve any solvents unlike the wet chemical process, and the thus eliminates environmental pollution.

In this work, the changes on the surface of PET polymer with ArF excimer laser have been investigated and analyzed. The aim of this work is to determine the ablation threshold, and how microstructures change on the PET film following an ArF laser irradiation by the laser fluence and the number of pulses, below and above the ablation threshold. The average of the apex angles of cones have been measured, so.

2. EXPERIMENTAL PROCEDURE

For all experiments, commercial stretched PET films with a thickness of 2mm were used. The samples were usually
exposed from 50 to 1500 pulses with 20ns of pulse width of an ArF excimer laser at 193-nm (LPX 220i, Lambda Physik) in air. The investigated fluences ranged from 5 to 100mJ/cm², i.e. well below and above the measured ablation threshold of 42.27 mJ/cm². In the experimental setup and the laser beam was passed from a 1cm x 1cm damper to reduce the size of output beam on the sample. By changing the amount of energy by adjusting the discharge voltage of laser and measuring energy by using an energy detector, various fluences were asked carefully. PET samples were submitted to laser radiation at normal incidence in atmospheric conditions and 1Hz pulse repetition frequency. 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 (50, 100, 250 and 500) were used. SEM investigations of the laser treated PET samples were performed for examination of the morphology of irradiated surface and conical structure with a QUANTA 200 instrument. The true cone-half angle was determined from the images after correcting for the SEM viewing angle, which was usually at 60° to the surface normal.

3. RESULT 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. For weakly absorbing polymers, it may take several laser pulses to reach the ablation threshold, while in strongly absorbing polymers, material removal can take place with the first pulse. Of course, it is dependent on the fluence of laser, so. PET is classified as a strongly absorbing organic polymer in the UV range, grouping it with other polymers such as Kapton™ [15].

When the fluence increases up to 50mJ/cm² and 100mJ/cm², changes are observed on the surfaces. To determine the ablation fluence threshold more accurately, as well as the effect of the increasing in the number of pulses that causes ablation of the surface to be examined. After increasing the fluence up to 50mJ/cm², which is until below the ablation threshold, some changes appearance can be evidenced (Fig. 4), where each structure seems to grow from a central point through branching. With the number of pulses more than 100,
conidial type structures are clearly evident on the surface. In fact for an energy density above the ablation threshold (100mJ/cm², Fig. 5), a progressive change in the morphology from a conidial structure (Figs. 4b, c, d) to conical structures (Fig. 5) has been observed. With capturing by tilting the sample (with an angle of 30 degrees), it can create cones clearly at this fluence. Cone structures formed on the surface of the polymer in the 50 pulse, by increasing the number of pulses, the number of cones increased and so in 1500 pulses, a very dense structure caused by cones and coned got bigger. By comparing of Figs. 4 and 5, it can be observed that the height of the cones is increases by the fluence while their numbers have been reduced.

The closed-packed cones with filamentary structures are seen at highest fluence near the center of the sample. The cones at the center can be more accurately described as cylinders capped by cones. Wispy structures were seen at some fluences. Pictures show that the apex angle of cones desires to a well-defined size. One possible effect, which can be observed for impurities in polymers, is the formation of cones microstructures in a well-defined fluence range. The cone formation is due to the higher threshold fluence of ablation compared to the pure polymer, while the apex angle of cones (θ) varies with the applied fluence (F) and ablation threshold (Fₐₗ) according to follow equation:

\[ \theta = 2 \sin^{-1} \left[ \frac{F_\text{ab}(1-R_\text{c})}{F(1-R(\theta))} \right] \]  (1)

Where R₀ and R(θ) are the surface reflectivities for incidence angles of 90° (normal to the surface) and θ degrees, respectively. Experiments on different polymers shows that there is a relation between the created structures on the surface of polymers and radiation conditions including fluence, the incident angle and wavelength of the laser [16]. In the range of various fluence, different structures are created on the surface. As discussed above, one of the most common structures is a conical formation that commonly happens in an identified fluence for each polymer. The size and shape of the conical microstructures strongly depended on the fluence. So that by increasing the fluence, the apex of cones become sharper and their angle decreases. So by measuring the apex angle of the cones in each fluence, it can be calculated the ablation threshold. Through created structures, one structure, for example, F = 100 mJ/ cm² with 100 pulses was selected as a sample and the apex angle of each cones was measured, Fig. 6.

The average of the apex angles, θₐᵥ, is 61.95 degree. By Fresnel equations, the R(θ) from the surface under the angle of θ = θₐᵥ can be calculated.

\[ R = \frac{\sin(\theta_2 - \theta_1)}{\sin(\theta_2 + \theta_1)} \]  (2)

For the normal angle to the surface, we have:

\[ R_0 = \frac{n_2 - n_1}{n_2 + n_1} = \frac{1.57 - 1}{1.57 + 1} = 0.0491 \]  (3)

Since irradiation was performed on air, therefore, n₁ = 1 and for PET, we have n₂ = 1.57. In addition, according to the Snell's law, the θ₂ ≈ 34.2° is obtained. From equation (2), the value of R is obtained about 0.219 (θ ≈ 61.95°). On the other hand, when the number of pulses). Finally the ablation threshold from equation (1) is obtained about 42.3 mJ/cm².

At above ablation threshold (Fig. 5), by increasing of the number of pulses, depending on the created structure has different effects on the surfaces and the number of cones is increased by enhancement of the number of pulses increases, the amount of ablated materials from the surface has been increased, and surface is covered with them and the energy distribution of the laser radiation on the surface is reduced. By development of ablation, the energy that reaches to the surface of polymer will be reduced until in a specified number of the laser pulses, this energy become less than the threshold and therefore ablation stops. In summary, there are three different zones performed in the interaction of laser- polymer that include in ablation threshold value, below threshold and above ablation threshold. In this area, different processes of interaction have been happened. Experiments show that the interaction of laser with sample under and around the threshold fluence causes chemical reactions on the surface and thus changes the characteristics of the surface. In this range, any ablation on the surface does not happen. By increasing the fluence up to the ablation threshold, the surface ablation starts but it is limited, its amount enhances with more fluence and develops to the bulk of the material. Changes in this area are often physically, such as changes in the morphology of the surface. Above the ablation threshold, depending on the conditions of experiment and the fluence, different structures are created on the surface, so that a number of them are shown in Figs. 4 and 5. When the fluence enhances, the escape of particles from the surface will be increased. This rate is more rapidly for smaller particles than that of heavier ones. By knowing the range of required fluence to create a microstructure can modified the surface of polymer for special applications.

4. CONCLUSION

In the process of irradiation on the surface of PET with laser pulses of ArF, the cone-shaped micro-structures were created. It was shown that by increasing in the number of pulses, basis diameter and height of the cone increases while their apex angle reduces and overall, cones become longer. The average of the apex angles of cones is about 62° and the ablation threshold is obtained about 42.3 mJ/cm².

REFERENCES


