ORDERLY PERFORATION OF POLYESTER FILMS BY EXCIMER LASER

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ORDERLY PERFORATION OF POLYESTER FILMS BY EXCIMER LASER

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ABSTRACT

The effects of 248 nm KrF excimer laser irradiation on combinations of different thickness PET films and different stainless steel mask mesh opening sizes were considered as a possible method to achieve different size perforations on different thickness PET films, in order to provide an effective and controllable perforation technology. Therefore, ablation behavior of PET films has been investigated for different laser energy fluence and number of laser pulses. Morphology of irradiated samples was observed by optical microscopy, and atomic forced microscopy to study topography and microstructures after laser ablation. An attempt has been made of correlate these findings with the orientation, strength and mechanical properties of the polymer.

The experimental results reveal that the percentage of perforation and the average perforated area increase with increasing number of pulses for all film thicknesses. The affected area, defined as the perforated area plus the heat affected zone (a black-char-region around the perforated area) decrease with increasing number of pulses. Due to the heat conducted from the steel mash wire, especially at cell corners, the perforation process seems to start initially at the cell corners. High laser fluence seems to lead to surface depressions due to thermal shock and surface stress waves along the process directions confirmed by tensile testing and x-ray analyses. The presence and the geometry of surface depressions were confirmed by atomic forced microscopy.

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TABLE OF CONTENTS

	Page
LIST OF TABLES	vii
LIST OF FIGURES	ix
CHAPTER	
I. INTRODUCTION	1
II. BACKGROUND AND LITERATURE SURVEY	3
2.1 Excimer Laser Basics	3
2.2. KrF Excimer Laser	5
2.3 Laser Ablation	7
2.4 Materials	14
2.5 Surface Modification BY EXcimer Laser Irradiation	17
III EXPERIMENTAL.....	19
3.1 Materials	19
3.2 Film Characterization	20
3.3 Film Treatment	22

3.4 Film Morphology	23
IV RESULTS AND DISCUSSION.....	25
4.1 Orientation Measurement	25
4.2 Mechanical Properties	29
4.3 Ablation Characteristics	31
4.4 Thermal Properties	35
4.5 Film Morphology.....	38
4.6 Heat Transfer Behaviors	45
V CONCLUSIONS.....	49
REFERENCES	51
APPENDICES.....	56
APPENDIX A TABLES AND FIGURES.....	57
APPENDIX B ORIENTATION FACTOR CALCULATION.....	71

LIST OF TABLES

Table	Page
3.1 Parameters of T316 Stainless (T316L) and PET films.	19
4.1 d-spacing and diffraction angle for PET lattice planes	26
4.2 Tensile Strength, Failure Strain and Young's Moduli for 124 μm thick PET Films	30
4.3 Tensile Strength, Failure Strain and Young's Moduli for 72 μm thick PET Films	30
4.4 The Data of 124 μm Film under 400 mJ/cm^2	36
A.1 Perforation and Affected Area Data for 124 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 43 μm Mesh	57
A.2 Perforation and Affected Area Data for 124 μm Thick Film Treated by 800 mJ/cm^2 Fluence Using 43 μm Mesh	58
A.3 Perforation and Affected Area Data for 124 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 43 μm Mesh	58
A.4 Perforation and Affected Area Data for 124 μm Thick Film Treated by 200 mJ/cm^2 Fluence Using 43 μm Mesh	59
A.5 Perforation and Affected Area Data for 124 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 30 μm Mesh	59
A.6 Perforation and Affected Area Data for 124 μm Thick Film Treated by 800 mJ/cm^2 Fluence Using 30 μm Mesh	60

A.7 Perforation and Affected Area Data for 124 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 30 μm Mesh	60
A.8 Perforation and Affected Area Data for 72 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 43 μm Mesh	62
A.9 Perforation and Affected Area Data for 72 μm Thick Film Treated by 600 mJ/cm^2 Fluence Using 43 μm Mesh	63
A.10 Perforation and Affected Area Data for 72 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 43 μm Mesh	63
A.11 Perforation and Affected Area Data for 72 μm Thick Film Treated by 200 mJ/cm^2 Fluence Using 43 μm Mesh	64
A.12 Perforation and Affected Area Data for 72 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 30 μm Mesh	64
A.13 Perforation and Affected Area Data for 72 μm Thick Film Treated by 600 mJ/cm^2 Fluence Using 30 μm Mesh	65
A.14 Perforation and Affected Area Data for 72 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 30 μm Mesh	65
A.15 Perforation and Affected Area Data for 72 μm Thick Film Treated by 200 mJ/cm^2 Fluence Using 30 μm Mesh	66

LIST OF FIGURES

Figure	Page
2.1 Lasing wavelengths (lower scale) and corresponding photon energy (upper scale) of different excimer lasers. The solid blocks indicate commercially important wavelengths.....	4
2.2 Internal energy of rare-gas halide molecule in excited and ground states.	5
2.3 The photo of experimental apparatus. a. KrF excimer laser; b. energy-meter(MAX 400); c. display of energy-meter; d. focus lens; e. tube to vacuum pump; f. mask and sample.....	6
2.4 The hypothetical interaction process of a UV laser pulse with polymer.	8
2.5 Schematic of photochemical model of laser ablation phenomenon.	10
2.6 The schematic of thermal model of laser ablation phenomenon.	12
2.7 Two – strage Polymerization Mechanisms of PET.....	15
2.8 The Schematic of wire cloth. (a) Wire cloth mesh count shown as two digits (i.e. 3X3) indicates the number of openings per inch; (b) Mesh opening size; (c) Wire diameter.	16
2.9 UV degradation schemes for PET material	17
3.1 The schematic of DSC sample.	21
3.2 (a) Sample measurement directions for tensile testing; (b) Schematic drawing of dumbbell shaped test specimen.....	22
3.3 The schematic diagram of sample (not to scale).	23
3.4 The schematic of scanning position of AFM.....	24

4.1 WAXS 0° stage film photographs for (a) machine direction, and (b) transverse direction of PET film.	25
4.2 2θ scan patterns for PET film, (a) Machine direction; (b) Transverse direction.	26
4.3 The orientation triangle diagram for the PET film samples. The directions are also shown.....	28
4.4 Strain-stress curves for PET films of (a) 124 μm and, (b) 72μm thick sample films. All three directions are shown.	30
4.5 (a) Perforated part of a mesh-cell; (b) Affected part of a mesh-cell.....	31
4.6 Variation of percent of perforated on irradiated film (124 μm) with different numbers of pulses. The mask mesh opening size is 43 μm. The effect of fluences are also shown.....	32
4.7 Variation of perforation area per hole on irradiated film (124 μm) with number of pulses. The mask mesh opening size is 43 μm. The effect of fluence and the fitted curves are also shown.	33
4.8 Variation of affected area per cell on irradiated film (124 μm) with number of pulses. The effect of mask mesh opening size is 43 μm. The fluence is also shown.	34
4.9 Variation of perforation percentage on irradiated film (124 μm) with number of pulses. The effect of mask mesh opening size is also shown. The energy fluence is 1000 mJ/cm ²	52
4.10 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 400 mJ/cm ² fluence.....	36
4.11 Variation of crystallinity on irradiated film (124 μm) with number of pulses. The effect of mask mesh opening size is also shown. The fluence is 400 mJ/cm ²	37
4.12 Pictures of film surfaces on the irradiated side, taken by optical microscope at 20X magnification. The numbers under each picture refer to: <i>Fluence – Film Thickness – Mesh Size – Number of Pulses</i>	38

4.13 Pictures of film surfaces on the irradiated side, taken by optical microscope at 20X magnification after irradiation using different fluences. The numbers under each picture refer to: Fluence – Film Thickness – Mesh Size – Number of Pulses, respectively.	39
4.14 Tapping mode AFM images of height and phase for the three positions. Three-dimensional views for each position are shown in: (A.2, B.2, C.2), and section analysis of each position are shown in: (A.3, B.3, C.3).	44
4.15 Pictures of film surfaces on the back side, taken by optical microscope with at 20X magnification: (a) 124 μm film thickness and 43 μm mesh size with 240 pulses. The energy fluence is 1000 mJ/cm^2 ; (b) 72 μm film thickness and 43 μm mesh size with 225 pulses. The energy fluence is 400 mJ/cm^2	45
4.16 The heat transfer model used to represent laser irradiated metal-mesh/PET film system: (a) Full view of model; (b) Side view of isothermal contours and heat flux; (c) Top view of isothermal contours and heat flux; (d) Version view of isothermal contours and heat flux.	47
A.1 Variation of percent perforated area for 124 μm film irradiated with different numbers of pulses. The mask mesh opening size is 30 μm . The effect of fluence is also shown.	61
A.2 Variation of perforated area per hole on irradiated film (124 μm) with number of pulses. The mask mesh opening size is 30 μm . The effect of fluence is also shown.	61
A.3 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 800 mJ/cm^2 fluence.	62
A.4 Variation of percent perforated area for 72 μm film irradiated with different numbers of pulses. The mask mesh opening size is 43 μm . The effect of fluence is also shown.	66
A.5 Variation of perforated area per hole on irradiated film (72 μm) with number of pulses. The mask mesh opening size is 43 μm . The effect of fluence is also shown.	67
A.6 Variation of percent perforated area for 72 μm film irradiated with different numbers of pulses. The mask mesh opening size is 30 μm . The effect of fluence is also shown.	67

A.7 Variation of perforated area per hole on irradiated film (72 μm) with number of pulses. The mask mesh opening size is 30 μm	68
A.8 The effect of mask mesh opening size on the variation of percent perforation for 72 μm film irradiated with different number of pulses using 1000 mJ/cm^2 fluence.....	68
A.9 The effect of mask mesh opening size on the variation of percent perforation for 72 μm film irradiated with different number of pulses using 600 mJ/cm^2 fluence.....	69
A.10 The effect of mask mesh opening size on the variation of percent perforation for 72 μm film irradiated with different number of pulses using 400 mJ/cm^2 fluence.....	69
A.11 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 200 mJ/cm^2 fluence.....	70

CHAPTER I

INTRODUCTION

Although the plastics industries have existed for about half-century, they have grown at an enormous rate, extending into many fields including food, electronics, automobiles and other manufacturing industries. With the growth of polymer industries, surface modification methods have gained more attention. The purpose of surface treatment is usually to modify the surface layer of polymer by inserting some functional group and inducing roughness on the surface to improve its wettability, printability, and its adhesion to other polymers or metals. One of the distinguished new technologies used for these purposes is excimer laser.

Excimer laser was first developed in 1975 as the most powerful members in the UV laser family. In 1982, Srinivasan and his colleagues developed the UV induced removal of thin layers of polymers using intense irradiation by excimer laser^{[1][2]}. Those discoveries stimulated scientific interest in physics and chemistry of excimer laser ablation process on polymer surfaces, and experiments have been extended to many polymers with different excimer lasers by many researchers during the past twenty years^{[3][4][5][6][7][8][9][10][11][18]}. Despite the high level of research and application activities, the nature of UV laser ablation of polymers is far from being fully understood. Various structural modifications may be induced on material surfaces upon excimer laser irradiation.

Laser ablation has distinct advantages over other means for surface alteration of polymeric materials due to high resolution, no thermal side effect, discrete surface alteration and so forth. One great advantage of excimer laser treatment is the capability it offers for machining or removing (ablating) layers from surfaces of materials with very little thermal damage to the bulk. This is possible with most polymers due to the fact that they have high absorption coefficients for UV light along with low heat conduction properties. Thus, excimer laser applications have extended into the medical fields such as eye surgery, tattoo removal, etc.

In this research, the pulsed UV laser ablation of two different thickness PET films was studied using two different sizes of mesh-masks, and by changing the laser energy fluence and the number of pulses. The percentage of laser ablation-induced perforation and perforation area are important physical quantities need to be analyzed for membrane applications. These laser effects were correlated with orientation, residual stress, heat transfer and mechanical properties of the PET films and the stainless steel mesh-masks used.

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Excimer Laser Basics

The name excimer comes from excited dimer, a class of molecules formed by the combination of two identical constituents in the excited state. The excimer laser as the most powerful member of ultraviolet (UV) laser family, was invented in 1970 by N.G. Basov et al, as consisting of a xenon dimer (Xe_2) excited by an electron beam to give stimulated emission at 172 nm wavelength^[12]. However it is only thirty years since UV lasers is reported to be used to process polymers. In the early 1980's, improvements on family of rare gas halide lasers grow its availability, involved one rare gas (argon, krypton, or xenon) atom and one halogen (fluorine or chlorine) atom and product under the appropriate conditions of electrical stimulation and high pressure. An overview of excimer lasers with their respective emission wavelengths is shown in Figure 2.1. Among those, the most commonly employed excimer laser gases are krypton fluoride (KrF , 248 nm), argon fluoride (ArF , 193 nm) and xenon chloride (XeCl , 308 nm).

Figure 2.1 Lasing wavelengths (lower scale) and the corresponding photon energies (upper scale) of different excimer lasers. The solid blocks indicate commercially important wavelengths^[13].

Excimer is a pseudo-molecule, which can only exist in an excited electronic state due to instability, and it dissociates into atoms in ground states 10 ns to several 10 ns in the UV spectral range^[12]. The laser light only can be emitted when two atoms are bound under excited state. And the molecules will be fall apart after they drop to the ground state. The potential well exists only for the excited state where the molecules can occupy couples of vibration levels. Figure 2.1 demonstrate the corresponding between internal energy and atomic distance.

Figure 2.2 Internal energy of rare-gas halide molecules in excited and ground states^[14].

2.2. KrF Excimer Laser

The first laser emission from excited KrF in an electric discharge was reported by Burnham and N. Djeu in 1976^[15]. In difference to many other laser types, the upper laser level is populated by a three-body collision, which involves Kr^+ , F, and buffer gas (typically, Ne or He). Furthermore, polymer applications of 248 nm Krypton Fluoride (KrF) excimer laser are much wider than other excimer lasers due to its higher output pulse energy and power. The production of KrF excimer laser light, which involves a large number of reactions, can be described as follows:

A fast high-voltage electric discharge initiates the excitation process to ensure the excited dimer formation as follows^[16]:

1. Electric current is used for ionization to obtain Kr^+ and highly electronegative F^- :

2. A reaction follows, producing an excited dimer at a high energy level:

Under high voltage, excited gas F strips electrons from Kr into a metastable state (KrF^*).

The KrF excimer laser emits when KrF^* molecules dissociate into atoms in the ground states. The output laser energy depends on the vibration level (the potential well).

Our excimer laser instrument is a Lambda Physik (now Coherent Inc., Santa Clara, CA) excimer laser LPX240 using KrF (248nm) gas, as shown in Figure 2.2.

Figure 2.3 The photo of experimental apparatus. a. KrF excimer laser; b. energy-meter(MAX 400); c. display of energy-meter; d. focus lens; e. tube to vacuum pump; f. mask and sample.

2.3 Laser Ablation

For excimer laser, one of the most widely studied is the laser ablation. And many applications are based on this phenomenon. In this section, the mechanism of laser ablation is discussed.

2.3.1 Ablation Threshold

The etch rate per pulse (denoted as x) is an important physical quantity relevant to ablation and its threshold value, as it represents the depth of material removed from the surface by each laser pulse. Such data is usually calculated using the average value of depth of the etch crater divided by the irradiated pulses. There are also more elaborate techniques, such as reported by P.E. Dyer^[17] to be engaged in determining the etch rate from each pulse. The threshold fluence F_T is the distinct fluence level corresponding to the onset of significant material removal. For a limited range of fluences above the threshold, the etch rate obeys Beer's law^[18]:

$$x = \alpha^{-1} \ln F/F_T \quad (2.4)$$

where, α is the absorption coefficient (cm^{-1}) determined at a certain laser wavelength.

2.3.2 Ablation Mechanism

A hypothetical interaction process of a UV laser pulse with a polymer (shown in Figure 2.4) was proposed by Srinivasan^[19], in 1994. The laser beam going through the mask strikes the surface of polymer. The backbones of long-chain molecule are broken by absorbing this stream of photons. And the polymer fragments are ejected which indicates the ablation phenomenon. However, ablation depth does not strictly depend on the absorption coefficient due to the penetration of photons are logarithmically declining with time. Actually, the exact mechanism of laser ablation on polymer by which this happens

is a very complex process and is still the topic of debates. There are several working models proposed to explain the mechanism of laser ablation^{[18][20][21][22][23][24][25]}. Among those, three specific models can be considered, photochemical model, thermal model, and photochemical – thermal model.

Figure 2.4 The hypothetical interaction process of a UV laser pulse with polymer^[19].

- Photochemical Model

Photochemical ablation is also known as ablative photo-decomposition which is termed by Srinivasan^[26]. He proposed the ablation process can be explained by which incident photons directly break the main chain bonds due to its extremely high energy of UV lasers with the absence of significant thermal damage. Decomposition reactions would take place mainly from electronically excited states and repulsive forces between species would lead to their rapid expulsion from surface. Energy absorbed in this bond-breaking process would restrict the temperature rise and the extent of thermal damage to the substrate.

A single pulse threshold is assumed in this model so that n bonds per unit volume must be broken to achieve material removal. The required fluence is estimated by equation 2.5^[17]:

$$F_n = nh\nu/\eta\alpha(1 - R) \quad (2.5)$$

where, η is the quantum yield for chain scission, $h\nu$ is the photon energy, which is assumed to exceed the bond energy of the polymer chain, and R is the surface reflection loss. Purely photochemical model has met with only limited success because of its failure to confirm the dominance of a fluence rather than irradiance threshold^[27] and its inability to quantify thresholds to compare with experimental data^[28]. Figure 2.5 shows the schematic of the photochemical model of laser ablation phenomenon.

Figure 2.5 The schematic of photochemical model of laser ablation phenomenon^[29].

In the above figure, the polymer is drawn as the ensemble of monomer units layer by layer, which are held together by strong attractive interaction^[30]. The assumption in this process is repulsive interaction among the reacted monomers. The reacted polymer etches layer by layer and ablates without melting the remainder of the sample.

- Thermal Model

A number of investigations have confirmed that a purely thermal process can produce effective polymer ablation^{[31][32]}. The thermal model assumes that the absorbed photon energy is transferred directly into excitation of lattice vibration,

which leads to thermally activated fragmentation of polymer on a shorter time scale compared to the laser pulse^{[32][33]}. This model is applicable for irradiation of the solid by laser light of insufficient energy to photo-chemically dissociate chemical bonds. A threshold-like behavior for polymer removal in this picture can be explained by noting that the rate k at which volatile products are formed by thermal decomposition will have a very strong temperature dependence. Assuming an Arrhenius expression is applicable, k will vary as equation 2.6^[34]:

$$k = A \exp(-E_A / RT) \quad (2.6)$$

where, T is the temperature, and A and E_A are the pre-exponential factor and the activation energy, respectively, for the decomposition path. An obvious threshold arises from the fact that k has to reach a sufficiently high value that measurable decomposition can occur on the time scale that the material remains hot. This heating time is defined by a combination of the laser pulse duration and the rate which heated surface layer cools via conduction to the bulk underlying polymer when the pulse terminates. The threshold fluence can then be estimated from equation 2.7^[34]:

$$F_T = C (T_D - T_R) / \alpha(1 - R) \quad (2.7)$$

where, T_D is temperature for measurable decomposition, C is the volumetric specific heat of the polymer, R is the surface reflection loss, and T_R is the initial surface temperature. In this equation, the heat loss due to conduction is ignored during the laser pulse duration and the thermal parameters of the polymer are considered to be constants. Figure 2.6 shows the schematic of thermal model for the laser ablation phenomenon.

Figure 2.6 The schematic of thermal model of laser ablation phenomenon ^[29].

In contrast to the photochemical model, only attractive potential is used in thermal model, assuming that the laser frequencies correspond to energies less than chemical bond strengths, and that, one photon is incapable of directly forcing the molecule to undergo an electronic transition. Therefore, the ablation of material corresponds to evaporation rather than a volume explosion. In addition, there is a time delay between when monomers in the first layer eject and when those in the deeper layers may reach the surface. Approximate 75% of the first layer of excited monomers, 30% of the second layer of excited monomers, and virtually none from the third and forth layers are ejected ^[29].

- Photochemical – thermal Model

Neither photochemical nor thermal model of ablation can exclusively explain the mechanism of polymer laser ablation. Both factors may potentially be important. It is reasonable to combine the above two models to form a promoted model, called photochemical – thermal model which can provide a better explanation for the laser ablation mechanism of polymers^[35]. According to this model, absorption of excimer laser radiation results in the excitation of chromophoric units in the polymer chains to the excited state. Deactivation processes are direct bond breakage in the excited electronic state (photo-dissociation) and electronic relaxation. The electronic relaxation induces heating of the surrounding material with the possibility of decomposition via thermal activation. Bond breakage leads to modified chromospheres with different cross-sections. Ablation occurs if the number of bonds broken directly or via thermal decomposition exceeds a threshold. The plume of ablated material expands three dimensionally and continues absorbing the laser radiation^[27]. V. Srinivasan et al^[36] reported that thermal effects were negligible at low fluence, while it became significant at higher fluences. At still higher fluences, the thermal rate reached a limiting value and the photochemical process again governed the process.

2.4 Materials

In this section, basic information of PET films and stainless steel meshes used in this study are introduced.

2.4.1 Polyester (Polyethylene terephthalate)

After its development in 1941 by John Rex Whinfield and his partners, PET has been considered as one of the most important commercial polyesters and is typically used in fiber, film and molded products.

2.4.1.1 The Synthesis of PET

Polyethylene terephthalate (PET) as a member of the polyester family of polymers, is a strong, stiff synthetic fiber and resin. Synthesis of PET is done by condensation/step-growth polymerization between ethylene glycol and terephthalic acid and by using aromatic sulphonates as catalysts. Due to the high melting point of terephthalic acid and its low solubility, the polymerization of PET can be completed by two-stage process, which is shown in Figure 2.7.

STEP 1

OR

STEP 2

Figure 2.7 Two-stage Polymerization Mechanisms of PET^{[37][38][39]}.

2.4.1.2 Crystallization Behavior of PET

Crystallization is very significant in affecting all mechanical and physical properties of PET just as for other types of semi-crystalline polymers. PET is a crystallizable polymer because of its regularity in chemical and geometric structures. Since the existence of benzene rings on the backbone, it's hard for PET to get an extremely high level of crystallinity. It's either in semi-crystalline state or in the amorphous state. Crystallinity in PET is usually induced by thermal crystallization and/or by stress or strain induced crystallization. Thermally induced crystallization occurs when the polymer is heated above its glass-transition temperature, T_g , and not quenched rapidly enough. In this condition the polymer turns opaque due to the spherulitic structure generated by thermal crystallization aggregates of un-oriented polymers^[40]. In stress-induced crystallization, stretching or orientation is applied to heated polymer and the polymer chains are rearranged in a parallel fashion and become closely packed^[41]. The crystallization process is composed of nucleation and spherulitic crystallization, and may occur at temperatures above T_g and below the melting point T_m ^[42]. Quenching the melt quickly results in a completely amorphous PET^[43].

2.4.2 Mesh

Wire cloth is a woven or welded material formed metal wire in a variety of opening sizes and wire diameters. The open area between wires is commercially called mesh count or mesh per linear inch. This is the critical information needed when ordering wire cloth. The mesh opening size can be computed by mesh count. Wire cloth is manufactured using a wide variety of materials, wire diameters, and mesh sizes to meet the demands of application. This metal fabric can take on numerous shapes to handle particular requirements. In this study, two different wire clothes are used, and the mesh counts are 325X325 and 500X500 (per inch, see Fig. 2.8) (obtained from TWP INC 2831 Tenth St. Berkeley, CA 94710 USA). The schematic of wire cloth is shown in Figure 2.8.

Figure 2.8 The Schematic of wire cloth showing: Wire cloth mesh count indicated by two digits (i.e. 3X3) and corresponding to the number of openings per inch (a); Mesh opening size (b); Wire diameter (c).

2.5 Surface Modification By Excimer Laser Irradiation

Controlled modification of polymeric properties induced by interaction of energetic particles beams, photons, and plasma has become a field of considerable technical importance. It can be used to improve adhesion properties of coatings as well as the wettability and printability of polymers by changing the morphology and chemical properties of the polymer surface.

2.5.1 Chemical Modification

In general, when a polymer's surface is irradiated by excimer laser in atmospheric environment, some parts of its chemical structure in the hydrocarbon group (CHX) may be altered to be more intensely polar, such as carbonyl (-C=O) and hydroxyl (-OH) group due to reactions with the environment^{[44][45]}. The most important reagent in atmosphere is oxygen. Oxidation can be initiated and accelerated by radiation (photo-oxidation) and thermal energy (thermal-oxidation), and leads to the degradation/decomposition of the polymer by bond dissociation, chain scission and cross linking^[46]. When PET film is irradiated by excimer laser, a series of degradation processes may occur as proposed by Marcotte^[47] and Day^[48], and shown in Figure 2.9.

Figure 2.9 UV degradation schemes for PET material

For the PET surface irradiated by 248nm KrF excimer laser, Watanabe et. al.^[49] suggested the formation of both OH and CHO groups. In his explanation, the formation of CHO group seems to be caused by photoreaction, while formation of OH group appears due to decomposition reaction from momentary heat at the time of laser irradiation.

2.5.2 Physical Modification

Besides chemical changes, laser ablated polymer surface also shows various physical modifications. As a result of photodecomposition of polymer induced by excimer laser irradiation, different microstructures have been reported on polymer surfaces. Although the relationship between final surface structure and affected parameters is not perfectly established, three major types of surface microstructures, well-defined cones, ripple-like and the so-called LIPSS (Laser Induced Periodic Surface Structure) structures developed on the excimer laser ablated polymers have drawn a lot of attention over the years^{[50][51][52]}.

In 1982, Srinivasan and Mayne-Banton^[53] first noticed the development of the complex two-dimensional ripple like structure on the surface of ablated PET films. They explained the formation of these structures seems to result from the high absorption coefficient at certain wavelength and high efficiency for photochemical bond breakage at photo energies. Thomas et al.^[54] assumed that this structure was induced by stretching or other orientation stress during the manufacturing process and was often in the form of channels or troughs aligned with or perpendicular to the stretching direction of the film.

CHAPTER III

EXPERIMENTAL

3.1 Materials

Two different types of meshes were used in this study: 325 mesh and 500 mesh, (T316 Stainless), obtained from TWP INC 2831 Tenth St. Berkeley, CA, 94710 USA. Polyethylene Terephthalate (PET) films, used in this research, were commercially obtained Mylar film of 4.8 mil (124 μm) X 50 in and 2.8 mil (72 μm) X 12in, respectively.

The physical properties of these materials are list in Table 3.1.

Table 3.1 Parameters of T316 Stainless (T316L) and PET films.

Martial	T316L	PET
Density ρ (g/cm^3)	7.99 ^[55]	1.45 ^[56]
Linear Temperature Expansion Coefficient $-\alpha$ (10^{-6} K^{-1}) ^[57]	16.0	59.4
Specific Heat c_p ($\text{J}/\text{g K}$)	0.5 ^[55]	2.1 ^[56]
Thermal conductivity κ $\text{W}/(\text{cm}\cdot\text{K})$	0.16 (373 K) ^[55]	0.0015 ^[56]
Thermal Diffusivity D (cm^2/s)	0.04	0.001 ^[56]
Optical penetration Depth α^{-1} (μm)	/	6.25 ^[58]
Heat Diffusion length $L_{25} = 2(Dt)^{-2}$ (μm) ($\tau=25 \text{ ns}$) ^[58]	0.63	0.16 ^[58]

3.2 Film Characterization

Before the laser treatment, the films were investigated by the characterization of WAXS, DSC, tensile testing.

3.2.1 Orientation Measurement

Wide angle x-ray scattering (WAXS) patterns were obtained to determine the orientation of PET films. Biaxial orientation factor of PET films was measured through a General Electric generator equipped with copper target tube and crystal monochromator. This equipment produced CuK α radiation at $\lambda = 0.15418$ nm. Operating conditions were set as 30 kV and 30 mA. Both types of films were cut and stacked with glue to insure that their thickness is larger than 200 μm for gaining reliable data.

3.2.2 Thermal Properties

Differential scanning calorimetry (DSC) was conducted using a TA Instrument 2920 MDSC V2.6A to characterize thermal properties of untreated and irradiated PET films. Samples of ~ 1 mg weight were carefully weighed and sealed in a hermetic aluminum pan (mass difference is ± 2 mg). The temperature was raised from 0 $^{\circ}\text{C}$ to 300 $^{\circ}\text{C}$ at an increasing rate of 10 $^{\circ}\text{C}/\text{min}$. The following equation (3.1) was used to calculate crystallinity of films.

$$\Phi_c(\%) = \frac{\Delta H_{\text{exp}}}{\Delta H^0} \times 100\% \quad (3.1)$$

where, ΔH^0 is the heat of fusion of 100% crystalline polymer, reported to be 125.5 J/g for PET^[59]. The samples used in DSC test were obtained from the parts of film which are very close to the affected region by laser, as illustrated in red shade position in Figure 3.1.

These regions were irradiated at different numbers of pulses using the same mask/mesh set up as used in perforation.

Figure 3.1 The schematic of DSC sample. Samples were irradiated at different numbers of pulses using the same mask/mesh set up as used in perforation.

3.2.3 Mechanical Properties

Mechanical investigations were performed on an Instron 5567 model tensile testing machine with a crosshead speed of 500 mm/min using a 1000N load cell. ASTM D412-TYPE A^[60] dumbbell shaped test specimens were loaded in machine direction (MD), transverse direction (TD) and at 45° to the MD and TD directions, as shown Figure 3.1.

(a)

(b)

Figure 3.2 (a) Sample measurement directions for tensile testing; (b) Schematic drawing of dumbbell shaped test specimen.

From the data of load and displacement at each point, stress-strain curves were obtained, and the Young's moduli were calculated for each direction.

3.3 Film Treatment

In this study, an Excimer Laser (LPX 2401) manufactured by Lambda Physik (Coherent, Santa Clara, CA) was used. The operational parameters of this machine are the energy level, fluence, pulse frequency, and the number of pulses. It is also capable of providing different wavelength lasers beams by changing the gas in the laser tube. For this research, 5% F_2/He , Kr and Ne were filled in the tubes to produce 248 nm wavelength KrF excimer laser beam. The concentration of fluorine must be controlled due to its toxicity. The laser beam area is 1.54 cm^2 (2.2 cm in width and 0.7 cm in height), and the energy confirms with edge-steepness profile for the beam cross – section is a Gaussian distribution^[61].

The laser energy is controlled by input voltage which can range from 16 kV to 26 kV. The pulse duration is 25 ns. The frequency of 1 Hz was used to treat samples to minimize

the thermal effect. In order to control the laser fluence more appropriately, voltage was kept in constant high, and the distance between focus lens and samples was adjusted to fit the need. The laser energy must be measured every time when starting the machine, as the lasing gas has limited life time. When the energy is too low, new gases need to be filled into tubes. Each sample was assembled in order of mask, mesh (four different sizes), and film (two different thicknesses). The sample assembly is shown in the Figure 3.3.

Figure 3.3 The schematic diagram of sample (not to scale).

3.4 Film Morphology

After laser treatment, light microscopy and AFM were applied to study the morphologies of film samples.

3.4.1 Light Microscopy

Irradiated films were observed and photographed by Leitz Laborlus 12 Pol s Microscope both with front and back views of the films, using a 20X optical objective. These photos were analyzed using ImageJ 1.X (by Wayne Rasband at NIH since 1997) in order to obtain measurements on sizes of perforated and heat – affected areas.

3.4.2 Atomic Force Microscopy (AFM)

The film morphology was also investigated by means of AFM (Atomic Force Microscopy). Samples were cleaned with compressed air to remove any fragments attached on their surfaces and traced in the tapping mode, at 0.25 Hz scan rate. The sample surface was monitored at 20X magnification. For laser alignment, signal spot was optimized approaching zero for both X and Y axis, meanwhile maximizing the signal intensity. After auto-tuning the cantilever, the probe was automatically directed to approach the film surface. Height images were obtained due to the presence of a constant force between tip and surface, which were translated and amplified into electrical signals, revealed through a computer. In order to explore the influence of laser energy on untreated film surface part, three main regions were scanned, as shown in the Figure 3.4.

800-124-30-3000

(Fluence – Film Thickness-Mesh Size - Number of Pulses)

Figure 3.4 The schematic of scanning positions of AFM.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Orientation Measurement

Wide angle x-ray scattering (WAXS) photographs for the sample films are shown in Figure 4.1. Diffraction patterns from (0 1 0) and (1 0 0) planes^[62] are observed in pictures of PET film in machine direction (Figure 4.1 (a)) and transverse direction (Figure 4.1(b)).

Figure 4.1 WAXS 0° stage film photographs for (a) machine direction, and (b) transverse direction of PET film.

PET has a triclinic unit cell structure^[63], and lattice constants are provided in *Polymer Data Handbook*^[59]. 2θ scan patterns for PET film samples, which are shown in Figure 4.2. The d-spacing for lattice plane can be calculated from equation (4.2) and the diffraction angles for lattice plane can be determined by Bragg's Law as shown in equation (4.1), since diffraction occurs only when Bragg's Law is satisfied.

$$n\lambda = 2d_{hkl}\sin\theta \quad (4.1)$$

where,

$$\frac{1}{d_{hkl}^2} = \frac{1}{(1+2\cos\alpha\cos\beta\cos\gamma-\cos^2\alpha-\cos^2\beta-\cos^2\gamma)} \left[\frac{h^2\sin^2\alpha}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2\sin^2\gamma}{c^2} + \frac{2hk}{ab}(\cos\alpha\cos\beta - \cos\gamma) + \frac{2kl}{bc}(\cos\beta\cos\gamma - \cos\alpha) + \frac{2lh}{ca}(\cos\gamma\cos\alpha - \cos\beta) \right] \quad (4.2)$$

Brag spacing and angle for (0 1 0) and (1 0 0) planes were calculated as shown in Table 4.1. The diffraction angles for lattice plane can be also determined by integral curve of intensity with 2θ , which is shown in Figure 4.2.

Table 4.1 d-spacing and diffraction angle for PET lattice planes

Reflection Index	d-spacing (Å)	Diffraction Angle (°)
(0 1 0)	5.19	17.06
(1 0 0)	3.96	22.43

Figure 4.2 2θ scan patterns for PET film, (a) Machine direction; (b) Transverse direction.

The orientation in the films was quantified by using the White – Spruiell biaxial orientation factors of crystallographic axes for crystalline polymers^[64], which are given as follows:

$$f_{1,j}^B = \overline{2\cos^2\phi_{1,j}} + \overline{\cos^2\phi_{2,j}} - 1$$

$$f_{2,j}^B = \overline{2\cos^2\phi_{2,j}} + \overline{\cos^2\phi_{1,j}} - 1 \quad (4.3)$$

where, 1, 2 represent the machine direction (MD), and transverse direction (TD), respectively. $\phi_{i,j}$ are the angles between the polymer chain direction i and crystallographic axis j which for PET could be defined as vectors normal to benzene rings in the backbone.

For this calculation, as a triclinic unit, PET can be treated as pseudo-orthorhombic in which the c-axis is along the chain axis, the a-axis is parallel to the phenyl ring normal, the b-axis is taken to be orthogonal to the ac plane. From Wilchinsky's treatment^[65] to the pseudo – orthorhombic unit cells, we can get:

$$\begin{aligned} \overline{\cos^2\phi_{i,c}} &= \frac{(f_1^2 - e_1^2)\overline{\cos^2\phi_{i,010}} - (f_2^2 - e_2^2)\overline{\cos^2\phi_{i,100}} + e_1^2 f_2^2 - e_2^2 f_1^2}{e_1^2(f_2^2 - e_2^2) - e_2^2(f_1^2 - e_1^2)} \\ \overline{\cos^2\phi_{i,a}} &= \frac{f_2^2 \overline{\cos^2\phi_{i,100}} - f_1^2 \overline{\cos^2\phi_{i,010}}}{f_2^2(e_1^2 - f_1^2) - e_2^2(e_2^2 - f_2^2)} \end{aligned} \quad (4.4)$$

where, i represents the major and minor symmetry axes, and e_1, e_2, f_1, f_2 are the direction cosines which are $\cos(21.65)$, $\cos(82.68)$, $\cos(68.36)$, and $\cos(7.32)$, respectively.

Insertion of the cosine values results in:

$$\begin{aligned} \overline{\cos^2\phi_{i,c}} &= 1 - 1.14126\overline{\cos^2\phi_{i,010}} - 0.85874\overline{\cos^2\phi_{i,100}} \\ \overline{\cos^2\phi_{i,a}} &= 1.16041\overline{\cos^2\phi_{i,100}} - 0.16041\overline{\cos^2\phi_{i,010}} \end{aligned} \quad (4.5)$$

The biaxial orientation factors were determined from equations (4.3) and (4.5), which can be graphical represented in orientation triangle in Figure 4.3,

Figure 4.3 The orientation triangle diagram for the PET film samples. The directions are also shown.

where, f_1^B , f_2^B represent uniaxial orientation with respect to the machine and transverse directions, respectively. The three apexes of triangle represent states of perfect uniaxial orientation with the (1, 0) and (0, 1) representing orientations in the plane of the film and (-1, -1) representing orientation perpendicular to the surface. Equal planar orientation is represented by point (1/2, 1/2) and all points along the base of triangle represent orientations within the plane. And the origin of the coordinate axes means the orientation is isotropic. All points on the altitude of dotted line represent states of equal biaxial orientation for which the orientation with respect to the machine direction and transverse direction is the same. The orientation factors of PET film for each axis were calculated (the calculation is attached in Appendix B) and shown in Figure 4.3. It is seen that orientation factors of three axes all fit the dashed line which represents equal biaxial state. In this case, the film can be treated as biaxially stretched.

4.2 Mechanical Properties

In general, stress-strain behavior of polymers depends largely on molecular conformation states in their amorphous and crystalline regions. The stress-strain curves obtained by tensile testing for two types of PET films are presented in Figure 4.3(a) (b), respectively. The stress increases sharply initially in the elastic region, where the Young's Moduli are obtained, and then decreases slightly after the yield point. Strain hardening due to molecular orientation is also observed with secondary increases in stress levels at higher deformation levels. Usually, a necking phenomenon will occur after yield point as a result of reducing width of sample under rising strength, as observed in MD and 45° directions. Tendency of TD behavior is close to the true stress-strain curve.

(b)

Figure 4.4 Strain-stress curves for PET films of (a) 124 μm and, (b) 72 μm thick sample films. All three directions are shown.

Table 4.2 Tensile Strength, Failure Strain and Young's Moduli for 124 μm thick PET Films

Direction	Failure Strain (mm/mm)	Tensile Strength (MPa)	Young's Modulus (MPa)
MD	0.67 ± 0.12	123.85 ± 7.62	2644.86 ± 90.35
TD	0.54 ± 0.09	171.60 ± 11.42	2824.67 ± 67.65
45°	0.64 ± 0.21	128.47 ± 8.60	2468.75 ± 71.73

Table 4.3 Tensile Strength, Failure Strain and Young's Moduli for 72 μm thick PET Films

Direction	Tensile Strain (mm/mm)	Tensile Stress (MPa)	Young's Modulus (MPa)
MD	0.66 ± 0.11	139.43 ± 4.00	2909.64 ± 55.27
TD	0.57 ± 0.08	189.30 ± 7.83	3015.06 ± 54.21
45°	0.79 ± 0.18	132.51 ± 9.06	2737.66 ± 46.13

The tensile strength, failure strain and Young's Moduli for the three process directions for our 124 and 72 μm thick film samples are listed in Tables 4.2, and 4.3, respectively. Apparently, the Young's Modulus in transverse direction is slightly higher than that in machine direction for both thickness of PET films, which are assumed to be biaxially stretched during manufacture. And it is also confirmed by x-ray analysis.

4.3 Ablation Characteristics

Percentage of perforation and affected area are important results of laser ablation which are affected by energy fluence and number of pulses. These results were recorded and analyzed on photographs. All photos were taken by optical microscope using 20X magnification and analyzed by ImageJ 1.X software (Wayne Rasband at NIH). Perforation area means the opening area observed by microscope, and the affected area represent this opening area plus the black (char) area around it as shown in Figure 4.4(a), (b). Therefore, the percent perforation represents the perforation area in any cell divided by the area of the corresponding mesh-cell. The % Perforation data was obtained from the back sides of the films, whereas the affected area data was obtained from the front (irradiated sides of the films).

Figure 4.5 (a) Perforated part of a mesh-cell; (b) Affected part of a mesh-cell.

Figure 4.6 Variation of percent perforated area for 124 μm film irradiated with different numbers of pulses and evaluated from the back side of the film. The mask mesh opening size is 43 μm . The effect of fluence is also shown.

In Figure 4.6, perforation percentage increases apparently with the number of pulses, initially, until reaching a threshold when the perforation percentage becomes almost constant or rises slightly afterwards. Meanwhile, the critical point of pulse at which film started to perforation reduced and perforation area increased with the rising of energy fluence. And the some trend can be observed in perforation area vs number of pulses, shown in the figure 4.7

Figure 4.7 Variation of perforated area per hole on irradiated film (124 μm) with number of pulses. The mask mesh opening size is 43 μm . The effect of fluence is also shown.

However, the affected area behaves in opposite way, decreasing initially and remaining constant or decreasing slightly afterwards (Figure 4.8). The initial reduction increases with higher fluence values as the polymer chains tend to curl and shrink by absorbing energy.

Figure 4.8 Variation of affected area per cell on irradiated film (124 μm) with number of pulses. The data shown was evaluated from the front side of the film. The effect of mask mesh opening size is 43 μm. The fluence is also shown.

We know that the, thermal conductivities of mesh and film are 0.16 and 0.0015, respectively (Table 3.1). We note that the laser pulse duration time is 25 ns and the pulse interval (frequency) is 1 second, which means the interval is 4×10^8 times longer than the pulse duration, and both the mesh and the film have abundant time for heat conduction.

On the other hand, mesh opening size is another significant effect factor can't be ignored. In the Figure 4.9, the critical pulse where started to be opening for 30 μm mesh is less than that of 43μm mesh, even though the irradiated film is exactly same. And this phenomenon can be observed either different energy fluences or different film thickness. Since both mesh and film have enough time for heat conduction, a temperature difference is created between the metal mesh and the PET film due to the difference in their specific heats (Table 3.1). Thus, heat flows from the mesh to the film. Obviously, 30 μm mesh is knitted tighter than 43μm mesh, which means the higher knitting tightness is, the larger the heat transfer affects.

Figure 4.9 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 800 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

All measured data listed in Tables A.1- A.15 show the perforation and affected area for different film thicknesses using different mesh sizes, under different fluencies and numbers of pulses. Figures A.1-A.11 illustrate the correlation between percentage of perforation, perforation area and affected area with energy fluence and the number of pulses. Those tables and figures are attached in appendix.

4.4 Thermal Properties

DSC (Differential Scanning Calorimetry) scans for 124 μm thickness film irradiated PET films. The crystallinity of irradiated films varied with different number of pulses is shown in the Table 4.19. The fluence is 400 mJ/cm^2 .

Table 4.4 The Data of 124 μm Film under 400 mJ/cm^2

Mask Mesh Opening Size (μm)	Number of Pluses	% perforation	% crystallinity (irradiated)
43	350	4.3	38.38
	360	3.92	38.82
	375	4.22	43.62
	390	3.72	46.43
	400	3.71	42.66
	800	5.88	37.51
	3000	5.84	39.06
	10000	6.13	42.57
30	260	1.95	39.44
	280	1.56	41.59
	290	0.67	42.72
	350	0.67	43.12
	400	1.08	44.48
	800	2.42	42.60
	3000	2.95	33.52
	10000	3.51	43.02

Figure 4.10 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 400 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

Figure 4.11 Variation of crystallinity on irradiated film (124 μm) with number of pulses. The effect of mask mesh opening size is also shown. The fluence is 400 mJ/cm^2 .

Comparing with the perforation behavior shown in Figure 4.10, the peak of crystallinity (Figure 4.11) appeared around the critical point (initial maximum) of percentage of perforation. This behavior may be related to the crystallization characteristic of PET. Although PET has a regular molecular structure, the existence of benzene ring in the backbone limits its crystallization. We also know that in addition to the thermal effect, mechanical stress also plays an important role in affecting crystallization. PET molecular chains tend to disorder when not under stress. When the film is heated by laser treatment and starts to perforate, the non-perforated part gains an increase in crystallinity due to the thermal effect, and while it still has its original crystalline structure induced by the original stretch process during manufacturing. After full perforation, the treated film loses its original crystalline structure while undergoing melting due to continuing energy absorption. We note that, as seen in Figure 4.11, after

reaching the maximum point, the level of crystallinity drops quickly to its lowest level (around 1000 pulses with 43 μm film, and ~ 3000 pulses with 30 μm film). Therefore, the slight upward trend in % perforation versus number of pulses behaviors we observe (Fig. 4.10) may be due to this abrupt drop in the crystallinity level of the films, which facilitates ablation.

4.5 Film Morphology.

Surface condition and the extent of perforation on films were examined by optical microscopy, as shown in Figures 4.12, 4.13.

Figure 4.12 Pictures of film surfaces on the irradiated side, taken by optical microscope at 20X magnification. The numbers under each picture refer to: *Fluence – Film Thickness – Mesh Size – Number of Pulses*.

Some lines were observed on pictures for the irradiated sides of samples emanating from around the heat-affected (black part, framing the perforated part) when the fluence was 800 mJ/cm^2 or higher (Figs. 4.12, 4.13), while the surface was much clearer under 400 mJ/cm^2 (Figs. 4.12, 4.13) for both mesh sizes (43 and 30 μm mesh), when compared at the same number of pulses.

Figure 4.13 Pictures of film surfaces on the irradiated side, taken by optical microscope at 20X magnification after irradiation using different fluences. The numbers under each picture refer to: Fluence – Film Thickness – Mesh Size – Number of Pulses, respectively.

AFM is a valuable tool to quantify the film surface micro-topography. Three different positions were scanned (Figure 3.4) to investigate the nature of the lines emanating from around the heat-affected (black) zones around the perforations, and the AFM images of each position are as shown in Figure 4.14(A - C).

(A.1)

(A.2)

(A.3)

(B.1)

(B.2)

(B.3)

(C.1)

(C.2)

(C.3)

Figure 4.14 Tapping mode AFM images of height and phase for the three positions. Three-dimensional views for each position are shown in: (A.2, B.2, C.2), and section analysis of each position are shown in: (A.3, B.3, C.3).

In above AFM images, those lines can be seen clearly. They are depressions appeared on the surface like valleys and not deep compared to the film thickness. For this treatment, laser beam is perpendicular to the surface of sample, reaching the front of mask first and straggling to the bottom of film. The position of experimental apparatus is shown in Figure 2.3, and the assembling of sample is shown in Figure 3.3. With the impact of high surface temperature and film thickness, the film surface tend to deform and extend on both directions due to the polymer properties, that is, high expansion coefficient of PET. Under the persisting strength induced by expansion, film surface begins to depressing along with carbonization of amorphous regions. Tensile testing and x-ray analysis revealed the transverse direction to have higher orientation in comparison to the machine

direction, and this direction seem to acquire more depression lines in comparison to the machine direction.

4.6 Heat Transfer Behaviors

Film perforation is affected by absorbing a certain amount of energy which serves to break molecular chains. This energy is delivered by the excimer laser but transmitted to the perforation site in two ways: the first is from the excimer laser beam directly as it impinges on the perforation site; the second component is transferred from the irradiated metal mesh in the form of heat conduction. This behavior can be expressed as:

$$E_{\text{film}} = E_{\text{laser}} + E_{\text{mesh}} \quad (4.6)$$

When the number of pulses is low, both of these components can significantly impact the heat distribution. It can be easily observed that opening appeared first at corner under lower fluence, and mesh opening size is large particularly, which is shown in Figure 4.15. Although 1 Hz of frequency is used in this study to minimize the thermal effect by increasing time for conductive and convective heat transfer processes, planar heat transfer, especially from the mesh to the film can't be completely ignored.

Figure 4.15 Pictures of film surfaces on the back side, taken by optical microscope with at 20X magnification: (a) 124 μm film thickness and 43 μm mesh size with 240 pulses.

The energy fluence is 1000 mJ/cm².; (b) 72 μm film thickness and 43 μm mesh size with 225 pulses. The energy fluence is 400 mJ/cm².

The photos in Figure 4.15 illustrate the condition of each film under the number of pulses at the initiation of perforation. The representative behavior is that openings first appear at the border. We observed this behavior not only on these photos but on many other photos for different film thickness and mesh opening size.

On the other hand, when the number of pulses is extremely high, the irradiation behavior is dominated by the energy absorbed from the laser beam directly as the energy transferred from the mesh wires by conduction is far less. This phenomenon can also be observed at high fluence on the AFM-scanned surfaces discussed earlier. The appearance of depression lines around the border and extending along the strength directions can be attributed to the high energy delivered by the laser beam.

If we assume that the laser light is homogeneously perpendicular to the film, then we can treat the first term in Equation (4.6) as a constant, E_c . Then, it is important to know the heat distribution on the film transferred from mesh. For this purpose, we used the simulation software COMSOL Multiphysics (by COMSOL, Inc.). First, we build the 3D model of the mesh and film using AutoCAD 2012 (by Autodesk, Inc.). This is done by, keeping the horizontal and vertical mesh wires in-plane, meanwhile, by doubling the thickness at each wire crossing points. The material types and the heat transfer in solids model can be loaded from the program. The top surface of this unit mesh is set as the only boundary heat source. The heat flow of this boundary condition is specified as 4000 W/m², and the program is executed providing us the results shown in Figure 4.16.

Figure 4.16 The heat transfer model used to represent laser irradiated metal-mesh/PET film system: (a) Full view of model; (b) Side view of isothermal contours and heat flux; (c) Top view of isothermal contours and heat flux; (d) Version view of surface temperature.

Our heat transfer model illustrated in Figure 4.16 (c) indicates that the temperature is decreasing with increasing distance from the mesh edges, as indicated by the lighter color corresponding to higher temperatures. Intuitively, a shape similar to a rounded square formed in the center of each cell has lower energy, and the rest of the mesh-opening (cell) part is treated as $E_{\text{mesh-max}}$. We must note, however, that the assumption described above is

idealized. In actuality, the parallel beam light is deflected after going through the focusing lens and the mesh-edge can't be optimally exposed to the laser light.

In conclusion, the energy absorbed at the center area is E_c , while the edges of the film get $E_{\text{mesh-max}}$. Then, there exists a region receiving the highest energy $E_c + E_{\text{mesh-max}}$, where the first perforation occurs as observed in Figure 4.15.

CHAPTER V

CONCLUSIONS

In this research, two different thickness PET films were treated by 248 nm KrF excimer laser through two different size mesh masks. From the tensile test, it is seen that the Young's Modulus in transverse direction is slightly higher than that in machine direction for both thicknesses of PET films, which are assumed to be biaxially stretched during manufacture. Higher Young's Modulus is obtained in the thicker PET film. The DSC analysis shows that the crystallinity of the PET films increase initially after laser treatment. This is because, the non-perforated part gains an increase in crystallinity due to the thermal effect. The film then undergoes melting during full perforation. .

The perforated area of film initially increases sharply with increasing number of pulses, which is may related to the decrease in crystallinity after the onset of perforation process. Then the perforation area reaches a plateau at high number of pulses, where the percentage of perforation keeps constant or rise slightly. The critical number of pulses triggering perforation decreases with increasing fluence, and larger perforated areas are formed with higher fluence at the same number of pulses. However, the affected area (perforated area plus the heat-affected zone) behaves in an opposite way, perhaps due to the polymer chains tending to curl and shrink after absorbing energy.

The data obtained from optical microscope and AFM reveal that the lines observed on the irradiated surfaces are depressions induced by thermal shock and surface stress

waves resulting from the laser wave interactions. We also note that these lines do not represent full through-the-thickness cracks.

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APPENDICES

APPENDIX A

TABLES AND FIGURES

Table A.1 Perforation and Affected Area Data for 124 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per-Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
230	43.10	11.40	2541.65	252.07	2.33
240	61.50	14.90	2467.22	221.56	3.33
245	130.30	78.40	2047.69	558.80	7.05
250	562.20	84.70	1622.38	124.84	30.41
260	594.20	64.90	1144.87	173.56	32.14
400	523.80	75.30	1344.92	186.66	28.33
800	657.30	88.90	1125.13	112.35	35.55
1500	579.89	84.05	1259.81	102.05	31.36
2000	604.02	80.13	1376.92	119.99	32.67
4000	689.40	80.10	1422.23	75.24	37.29
6000	673.42	101.13	1252.96	79.27	36.42
10000	720.49	109.98	1487.33	163.42	38.97

Table A.2 Perforation and Affected Area Data for 124 μm Thick Film Treated by 800 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
245	22.80	66.19	2453.38	401.14	1.23
250	25.92	72.25	2428.78	350.98	1.40
255	126.24	136.87	1870.09	414.85	6.83
260	209.00	195.36	2159.14	600.72	11.30
275	458.16	109.51	1322.72	174.25	24.78
290	446.94	133.61	1229.52	235.63	24.17
300	562.03	108.75	1927.57	139.95	30.40
400	533.81	110.63	1730.06	135.30	28.87
500	532.63	98.99	1439.25	156.09	28.81
800	578.26	110.66	1337.34	125.99	31.27
1500	501.80	151.36	1194.51	104.27	27.14
3000	487.66	95.77	1097.79	116.83	26.37
6000	694.84	136.31	995.55	151.69	37.58
10000	644.85	90.93	987.24	94.09	34.88

Table A.3 Perforation and Affected Area Data for 124 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
310	22.81	18.37	1677.63	238.18	1.23
315	38.71	45.41	1411.10	245.09	2.09
320	80.92	65.45	1624.19	346.09	4.38
330	159.33	159.33	1806.67	270.45	8.62
340	157.47	66.03	1356.54	265.56	8.52
350	297.26	66.02	1515.29	226.72	16.08
390	247.56	54.91	1447.32	151.53	13.39
500	270.87	64.38	1384.90	182.99	14.65
800	345.37	66.86	1589.43	125.12	18.68
1500	280.47	76.75	1223.28	242.23	15.17
3000	334.95	59.55	1279.53	217.39	18.12
6000	407.66	91.70	1191.97	168.60	22.05
10000	354.69	87.83	1191.45	190.55	19.18

Table A.4 Perforation and Affected Area Data for 124 μm Thick Film Treated by 200 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
430	5.12	3.74	1614.91	225.46	0.28
440	15.43	11.21	1550.40	219.83	0.83
450	48.96	31.45	1595.98	198.31	2.65
500	80.02	40.35	1330.98	159.45	4.33
600	75.67	43.06	1461.88	133.52	4.09
800	70.28	35.84	1554.34	121.44	3.80
1000	81.16	32.36	1295.08	142.20	4.39
1500	73.36	40.05	1231.07	112.62	3.97
3000	86.51	39.75	1355.13	145.54	4.68
6000	117.75	38.11	1324.58	144.74	6.37
10000	108.29	41.09	1382.22	163.84	5.86

Table A.5 Perforation and Affected Area Data for 124 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
200	16.62	12.18	831.58	76.85	1.85
210	14.76	18.11	816.41	195.52	1.64
220	64.75	15.32	721.46	41.93	7.19
300	96.27	13.32	762.44	69.77	10.70
400	103.57	16.79	685.03	63.53	11.51
500	115.42	11.66	546.04	88.19	12.82
800	108.50	13.23	702.32	80.44	12.06
1500	126.61	21.12	461.70	84.26	14.07
3000	117.58	13.48	474.64	79.06	13.06
6000	121.66	17.98	584.35	92.98	13.52
10000	128.48	30.76	565.50	83.65	14.28

Table A.6 Perforation and Affected Area Data for 124 μm Thick Film Treated by 800 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
205	15.29	12.14	741.45	80.50	1.70
220	39.49	9.57	641.22	91.35	4.39
250	44.85	13.22	589.78	65.21	4.98
300	45.21	15.22	564.31	113.38	5.02
400	55.15	9.99	660.73	60.47	6.13
500	47.58	12.35	479.30	84.64	5.29
800	45.84	11.53	641.37	55.76	5.09
1500	54.34	12.66	470.79	81.70	6.04
3000	73.69	18.22	512.61	74.75	8.19
6000	77.52	16.65	507.37	61.16	8.61
10000	86.17	20.17	481.67	110.52	9.57

Table A.7 Perforation and Affected Area Data for 124 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
270	3.02	5.41	750.79	46.58	0.34
280	3.84	3.96	881.28	88.12	0.43
290	12.83	4.88	827.24	87.13	1.43
300	33.94	8.17	823.12	45.11	3.77
350	41.37	8.06	801.19	46.53	4.60
400	52.75	9.05	758.51	37.53	5.86
500	47.50	12.65	833.06	44.29	5.28
800	61.12	11.43	804.56	44.74	6.79
1500	75.82	13.40	751.01	79.43	8.42
3000	73.91	13.88	746.21	62.54	8.21
6000	92.60	18.34	798.55	67.70	10.29
10000	88.62	11.24	705.11	104.98	9.85

Figure A.1 Variation of percent perforated area for 124 μm film irradiated with different numbers of pulses and evaluated from the back side of the film. The mask mesh opening size is 30 μm . The effect of fluence is also shown.

Figure A.2 Variation of perforated area per hole on irradiated film (124 μm) with number of pulses and evaluated from the back side of the film. The mask mesh opening size is 30 μm . The effect of fluence is also shown.

Figure A.3 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 1000 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

Table A.8 Perforation and Affected Area Data for 72 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
130.00	17.64	7.29	3219.77	258.03	0.95
135.00	35.89	33.61	2543.84	281.48	1.94
140.00	780.01	256.17	2311.59	415.24	42.19
150.00	906.99	165.62	2564.15	265.52	49.05
175.00	887.84	213.08	2396.62	354.97	48.02
200.00	825.75	171.54	2352.52	270.96	44.66
500.00	779.68	169.09	2586.15	281.84	42.17
800.00	1089.62	174.05	2804.37	364.50	58.93
1500.00	1045.47	247.54	3768.87	430.22	56.54
3000.00	848.86	190.57	2565.33	185.98	45.91

Table A.9 Perforation and Affected Area Data for 72 μm Thick Film Treated by 600 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
152.00	3.01	2.46	1731.88	273.57	0.16
155.00	168.40	239.63	1714.52	265.37	9.11
160.00	641.22	238.81	1989.26	295.38	34.68
200.00	773.22	128.06	1984.21	232.48	41.82
230.00	682.13	162.90	1952.76	318.25	36.89
500.00	723.78	140.11	1981.56	262.30	39.14
800.00	739.76	162.13	2078.09	477.48	40.01
1500.00	773.64	170.83	2117.23	386.84	41.84
3000.00	818.86	132.95	1995.20	159.58	44.29

Table A.10 Perforation and Affected Area Data for 72 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
225.00	31.29	18.39	1751.63	208.44	1.69
230.00	171.22	122.04	1863.67	229.23	9.26
240.00	296.34	112.84	1710.41	203.96	16.03
250.00	421.32	94.19	1900.52	215.33	22.79
300.00	481.81	106.70	1828.97	227.80	26.06
500.00	542.98	86.79	1675.54	254.28	29.37
800.00	416.60	113.58	1698.83	145.16	22.53
1500.00	463.56	110.99	1692.29	220.80	25.07
3000.00	485.93	132.81	1781.35	1781.35	26.28

Table A.11 Perforation and Affected Area Data for 72 μm Thick Film Treated by 200 mJ/cm^2 Fluence Using 43 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
235.00	12.61	14.44	1504.61	228.32	0.68
240.00	26.88	27.24	1386.70	197.87	1.45
245.00	51.09	47.38	1419.23	225.20	2.76
250.00	46.89	9.88	1340.90	226.92	2.54
260.00	131.48	61.96	1324.88	204.87	7.11
300.00	202.76	64.95	1433.87	213.49	10.97
500.00	171.23	59.46	1455.80	234.88	9.26
800.00	184.01	66.84	1301.59	241.09	9.95
1500.00	284.23	94.51	1623.16	162.00	15.37
3000.00	476.09	81.79	1659.95	213.45	25.75

Table A.12 Perforation and Affected Area Data for 72 μm Thick Film Treated by 1000 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
120.00	1.66	1.36	931.42	54.74	0.18
125.00	143.95	89.68	1057.62	73.95	15.99
130.00	122.44	50.94	928.34	125.03	13.60
135.00	198.27	45.62	1100.17	80.94	22.03
150.00	159.33	52.45	759.12	54.56	17.70
200.00	154.58	20.53	843.91	52.92	17.18
500.00	187.42	32.78	\	\	20.82
800.00	272.58	45.86	\	\	30.29
1500.00	248.04	28.71	\	\	27.56
3000.00	277.38	39.45	\	\	30.82

Table A.13 Perforation and Affected Area Data for 72 μm Thick Film Treated by 600 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
150.00	2.96	2.39	988.70	64.36	0.33
155.00	193.43	34.81	957.78	76.42	21.49
165.00	187.30	35.81	949.93	74.63	20.81
200.00	196.71	23.24	928.49	58.44	21.86
250.00	193.87	24.97	993.82	64.14	21.54
500.00	170.83	26.36	965.52	55.32	18.98
800.00	231.97	34.08	886.67	58.70	25.77
1500.00	220.19	34.81	893.72	59.91	24.47
3000.00	239.81	36.37	876.53	56.19	26.65

Table A.14 Perforation and Affected Area Data for 72 μm Thick Film Treated by 400 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
190.00	7.47	6.56	632.33	53.77	0.83
200.00	25.59	11.17	693.98	58.51	2.84
210.00	41.64	9.31	617.59	43.65	4.63
225.00	51.86	11.04	680.58	40.72	5.76
300.00	50.35	13.73	608.69	56.43	5.59
500.00	47.08	11.76	623.37	49.01	5.23
800.00	57.05	10.61	658.94	53.88	6.34
1500.00	49.47	8.56	641.54	54.68	5.50
3000.00	68.03	13.15	636.47	62.84	7.56

Table A.15 Perforation and Affected Area Data for 72 μm Thick Film Treated by 200 mJ/cm^2 Fluence Using 30 μm Mesh

Number of Pulses	Perforation Area per Hole (μm^2)		Affected Area per Cell (μm^2)		% perforation
	Average	St. Dv	Average	St. Dv	
210.00	5.82	4.97	469.49	34.75	0.65
220.00	26.81	8.57	501.30	36.21	2.98
230.00	43.80	9.80	631.51	40.50	4.87
240.00	46.60	5.32	596.30	39.72	5.18
250.00	46.83	10.09	584.96	42.54	5.20
300.00	49.01	6.17	597.39	37.98	5.45
500.00	42.90	11.36	572.00	34.36	4.77
800.00	43.98	10.43	538.72	42.41	4.89
1500.00	62.17	21.22	768.57	65.88	6.91
3000.00	67.69	16.40	665.77	43.32	7.52

Figure A.4 Variation of percent perforated area for 72 μm film irradiated with different numbers of pulses and evaluated from the back side of the film. The mask mesh opening size is 43 μm . The effect of fluence is also shown.

Figure A.5 Variation of perforated area per hole on irradiated film (72 μm) with number of pulses and evaluated from the back side of the film. The mask mesh opening size is 43 μm . The effect of fluence is also shown.

Figure A.6 Variation of percent perforated area for 72 μm film irradiated with different numbers of pulses and evaluated from the back side of the film. The mask mesh opening size is 30 μm . The effect of fluence is also shown.

Figure A.7 Variation of perforated area per hole on irradiated film (72 μm) with number of pulses and evaluated from the back side of the film. The mask mesh opening size is 30 μm .

Figure A.8 The effect of mask mesh opening size on the variation of percent perforation for 72 μm film irradiated with different number of pulses using 1000 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

Figure A.9 The effect of mask mesh opening size on the variation of percent perforation for 72 μm film irradiated with different number of pulses using 600 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

Figure A.10 The effect of mask mesh opening size on the variation of percent perforation for 72 μm film irradiated with different number of pulses using 400 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

Figure A.11 The effect of mask mesh opening size on the variation of percent perforation for 124 μm film irradiated with different number of pulses using 200 mJ/cm^2 fluence. The data shown was evaluated from the back side of the film.

APPENDIX B
ORIENTATION FACTOR CALCULATION

The Equations (4.3, 4.5) were used to calculate the biaxial orientation factors, and the calculation steps were shown as following.

For (010) plane, $\overline{\cos^2 \phi_{(010),1}} = 0.274498$, $\overline{\cos^2 \phi_{(010),2}} = 0.31366$.

For (100) plane, $\overline{\cos^2 \phi_{(100),1}} = 0.304612$, $\overline{\cos^2 \phi_{(100),2}} = 0.27450$.

Then

$$\overline{\cos^2 \phi_{c,1}} = 1 - 1.14126 \overline{\cos^2 \phi_{(010),1}} - 0.85874 \overline{\cos^2 \phi_{(100),1}} = 0.42514$$

$$\overline{\cos^2 \phi_{c,2}} = 1 - 1.14126 \overline{\cos^2 \phi_{(010),2}} - 0.85874 \overline{\cos^2 \phi_{(100),2}} = 0.40630$$

And

$$\overline{\cos^2 \phi_{a,1}} = 1.16041 \overline{\cos^2 \phi_{(010),1}} - 0.16041 \overline{\cos^2 \phi_{(100),1}} = 0.39443$$

$$\overline{\cos^2 \phi_{a,2}} = 1.16041 \overline{\cos^2 \phi_{(010),2}} - 0.16041 \overline{\cos^2 \phi_{(100),2}} = 0.26822$$

$$\overline{\cos^2 \phi_{b,1}} = 1 - \overline{\cos^2 \phi_{c,1}} - \overline{\cos^2 \phi_{a,1}} = 0.26541$$

$$\overline{\cos^2 \phi_{b,2}} = 1 - \overline{\cos^2 \phi_{c,2}} - \overline{\cos^2 \phi_{a,2}} = 0.32548$$

Then White-Spruiell biaxial orientation factors for c-axis can be calculated through:

$$f_{c,1} = 2\overline{\cos^2 \phi_{c,1}} + \overline{\cos^2 \phi_{c,2}} - 1 = 0.25659$$

$$f_{c,2} = \overline{2\cos^2 \phi_{c,2} + \cos^2 \phi_{c,1}} - 1 = 0.23775$$

Similarly, for a-axis and b-axis, we can obtain:

$$f_{a,1} = \overline{2\cos^2 \phi_{a,1} + \cos^2 \phi_{a,2}} - 1 = -0.11290$$

$$f_{a,2} = \overline{2\cos^2 \phi_{a,2} + \cos^2 \phi_{a,1}} - 1 = -0.15413$$

$$f_{b,1} = -0.14370$$

$$f_{b,2} = -0.08363$$

where, 1, 2 represent the machine (MD) and transverse (TD) directions respectively. And, c-axis is along the molecular chain axis; a-axis is parallel to the phenyl ring normal; b-axis is perpendicular to the a-c plane.