Femtosecond laser micromachining of polymer surfaces

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Abstract

Femtosecond (fs) laser micromachining is a single-step, contactless surface texturing method which can create hierarchical structures that present both micro- and nanoscale roughness. While fs laser-induced structures have been extensively studied on metals, very few publications have investigated their formation on polymer surfaces. It has recently been shown that homogeneous fs irradiation of a poly(tetrafluoroethylene) surface leads to the formation of a high surface area porous structure. Such a structure could be highly beneficial for several applications such as self-cleaning materials and biomedical implants. However, as of yet, no basis for the optimization of this novel topology exists since its optical and chemical properties and the mechanism behind its formation have not been investigated. Thus, in this thesis, a detailed investigation and characterization of femtosecond laser-induced structures on polymer surfaces was performed.

By fitting several absorption models to ablation data, porous structure formation was determined to form as a consequence of explosive boiling and was observed to depend on the threshold fluence at machining conditions. For polymers with a sufficiently high threshold fluence, a minority of the incoming energy is converted into material ionization. Thus, the surface melt layer heats above the critical temperature for phase explosion and homogeneous bubble formation occurs. The quenching of the melt layer in between consecutive pulses leads to the formation of pores which are a remnant of the volume occupied by the bubbles during explosive boiling. Spectroscopy and X-ray photoelectron spectroscopy characterization at different wavelengths helped identify the parameters that affect the threshold fluence through incubation effects. Higher threshold fluences and lower incubation coefficients were observed during near-infrared irradiation as opposed to ultraviolet irradiation. This behavior at longer wavelengths was attributed to a shift from a multiphoton absorption mechanism at low pulse numbers to a linear absorption mechanism at higher pulse numbers. This effect was observed to be more significant for polymers that are susceptible to photooxidation.

Crystallographic evidence of explosive boiling was measured by grazing incidence X-ray diffractometry. For high density poly(ethylene), laser micromachining was observed to induce a local decrease in crystallinity and the appearance of a monoclinic phase that is typically only stable

at high temperatures and pressure. This confirmed that fs laser-induced polymer structures form from a quenched melt layer. In addition, the effect of viscoelastic melt properties on pore size was investigated. It was observed that for higher molecular weights (and thus higher viscosities), smaller pore sizes are achieved due to a decreased bubble growth rate during explosive boiling.

Finally, a novel atmospheric pulsed laser deposition setup for the incorporation of nanoparticles into laser induced porous structures was developed. Through this technique, hydrophilic titanium oxide nanoclusters were incorporated into porous poly(ethylene terephthalate). By controlling the extent of nanoparticle coverage through the operating fluence, tunable wettability was achieved. Thus, this technique allows the optimization of fs laser induced structures for specific applications without compromising the porous topology.

Abrégé

Le micro-usinage au laser femtoseconde (fs) est une méthode de texturation de surface sans contact qui peut créer des structures à rugosité hiérarchique (micrométrique et nanométrique à la fois). Tandis que les structures induites par les lasers fs ont été amplement étudiées sur les métaux, très peu de publications se sont intéressées à leur formation sur les surfaces de polymères. Récemment, il a été démontré que l'irradiation fs d'une surface de poly(tétrafluoroethylène) entraîne la formation d'une structure poreuse de grande surface. Une telle structure peut être avantageuse dans plusieurs applications comme les matériaux auto-nettoyants et les implants biomédicaux. Cependant, on ne sait pas si cette structure est reproductible sur d'autres polymères. D'autant plus que ni ses propriétés optiques et chimiques ni le mécanisme de sa production ne sont encore connues. Par conséquent, dans cette thèse, un travail détaillé d'investigation et de caractérisation a été accompli sur les structures induites par laser fs sur les surfaces polymériques.

En ajustant plusieurs modèles d'absorption aux données d'ablation, on a constaté que la formation de structures poreuses se produit à la suite d'une ébullition explosive et dépend du seuil de fluence aux conditions d'usinage. En ce qui concerne les polymères ayant un seuil élevé de fluence, une petite partie de l'énergie entrante est convertie en ionisation du matériau. Donc, la couche de surface en fusion chauffe au-delà de la température critique de l'ébullition explosive causant une nucléation homogène de bulles. Le refroidissement rapide de la couche en fusion entre deux impulsions consécutives entraîne la formation de pores qui correspondent au volume occupé par les bulles durant l'ébullition explosive. La caractérisation par spectroscopie UV-VIS et photo électronique par rayons X à deux longueurs d'ondes différentes a permis d'identifier les paramètres qui affectent le seuil de fluence à travers les effets d'incubation. Des seuils de fluence plus élevés et des coefficients d'incubation plus bas ont été observés durant l'irradiation infrarouge en comparaison avec l'irradiation ultraviolette. Ce comportement durant l'irradiation infrarouge a été attribué à la transition d'une absorption multiphoton pour un nombre réduit d'impulsions à une absorption linéaire pour un nombre élevé d'impulsions. On a constaté que cet effet était plus prononcé pour les polymères susceptibles de photo-oxydation.

L'ébullition explosive a été mise en évidence grâce à une étude cristallographique par diffractométrie de rayons X à incidence rasante. Avec du poly(éthylène) de haute densité, le micro

usinage laser a provoqué la baisse locale du niveau de cristallinité et l'apparition d'une phase monoclinique qui n'est habituellement stable qu'à haute température et pression élevée. Cela a confirmé que les structures produites par le laser fs se forment à partir d'une couche en fusion rapidement refroidie. De plus, nous avons étudié l'effet des propriétés viscoélastiques du polymère en fusion sur la taille des pores. Nous avons constaté qu'avec de plus grandes masses moléculaires (et donc des viscosités plus élevées), on obtient des pores de plus petite taille à cause de la diminution de la vitesse de croissance des bulles durant l'ébullition explosive.

Enfin, une nouvelle technique de dépôt par ablation laser à impulsions a été conçue pour incorporer des nanoparticules à l'intérieur des structures poreuses. Grâce à cette technique, de l'oxyde de titane hydrophile a été incorporé dans du poly(téréphthalate d'éthylène) poreux. En contrôlant l'étendue de la couverture de la surface par les nanoparticules au moyen de la fluence, la mouillabilité de la surface a pu être contrôlée. Par conséquent, cette technique permet l'optimisation des structures induites par laser fs pour des applications spécifiques sans compromettre la topologie poreuse.

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Nomenclature and list of abbreviations

Symbol	Description
n _e	Free electron density
t	Time
\dot{n}_{mp}	Rate of multiphoton absorption
δ	Impact probability between a free electron and an atom
$ ilde{\delta}$	Impact probability between a high kinetic energy free electron and an atom
n_k	High kinetic energy free electron density
<i>t_{MRE}</i>	Characteristic time for avalanche ionization
e_{ph}	Electron-phonon coupling constant
$ au_{relax}$	Characteristic relaxation time for thermal equilibration
Ci	Specific heat of component <i>i</i>
Т	Temperature
T_c	Critical temperature
F_{0}	Single pulse peak fluence
F_{th}	Threshold fluence
E	Laser pulse energy
Р	Laser Power
ω_0	Beam spot diameter
E_p	Photon energy
E_g	Bandgap Energy
h	Planck's constant
С	Speed of light
λ	Wavelength

Nomenclature (in order of appearance)

λ_c	Cutoff wavelength
N	Pulse number
ξ	Incubation coefficient
C_h	Heat capacity
β	Proportion of absorbed light
δ_T	Thermal diffusivity
t_h	Sample thickness
f_p	Repetition rate
F_d	Threshold fluence of a defect
F_i	Threshold fluence of a defect-free surface
ξ́d	Incubation coefficient of a defect
ξ_i	Incubation coefficient of a defect-free surface
П	Probability of irradiating a defect with a fluence above its threshold
σ	Surface density of defects
v	Velocity
PPS	Pulse-per-spot number
d	Ablation depth per pulse
Δx	Horizontal distance between two consecutive pulses
Δz	Vertical distance between two consecutive lines
${\Phi}$	Overlap
D	Ablated width
α	Absorption coefficient
$lpha_{e\!f\!f}$	Effective absorption coefficient
т	Order of absorption
α_m	<i>m</i> -th order absorption coefficient
Ι	Laser intensity
Z	Depth into the bulk
τ	Laser pulse duration
Λ	Period
θ	Angle
l_{ab}	Ablated depth

lms	Microstructure thickness
l_{tot}	Total affected depth
r	Box size
λ_{lac}	Lacunarity
s _k	Standard deviation of foreground pixel distribution
\overline{k}	Mean of foreground pixel distribution
Θ	Spatial heterogeneity index
M	Smaller dimension of analyzed image
<i>0</i>	Normalized spatial heterogeneity index
M_w	Weight average molecular weight
ρ	Density
γ	Strain rate
γo	Strain amplitude
ω	Angular frequency
η	Dynamic viscosity
η^*	Complex viscosity
G'	Storage modulus
G"	Loss modulus
l_{cx}	Horizontal chord length
l_{cy}	Vertical chord length
R	Bubble radius
P_g	Pressure inside a bubble
P_∞	External pressure
η_l	Liquid kinematic viscosity
γ*	Surface tension
E_{σ}	Elastic stress
$ heta_Y$	Young's contact angle
θ^*	Apparent contact angle
r*	Roughness ratio
f_i	Area fraction of component <i>i</i>
d^*	Target-substrate distance

n	Overscan number
$ heta_A$	Advancing contact angle
θ_R	Receding contact angle
L	Maximum plasma plume length
γh	Specific heat ratio
V	Plasma volume at the end of laser pulse
a	Focused beam spot area
A	Plasma plume expansion geometrical factor

Abbreviation	Description
3D	three dimensional
AFM	atomic force microscopy
AFP	accumulated fluence profile
ARCA	advancing and receding contact angle
COP	cyclic olefin polymer
СТ	computed tomography
EGDMA	ethylene glycol dimethacrylate
fs	femtosecond
GIXRD	grazing incidence x-ray diffractometry
HAZ	heat affected zone
HDPE	high density poly(ethylene)
HT-GPC	high temperature gel permeation chromatography
IR	infrared
LDPE	low density poly(ethylene)
LIPSS	laser-induced periodic surface structures
PA	poly(amide)
PC	poly(carbonate)
PCL	poly(caprolactone)
PDMS	poly(dimethyl siloxane)
PE	poly(ethylene)
PEEK	poly(ether ether ketone)
PES	poly(ether sulfone)
PET	poly(ethylene terephthalate)
PI	poly(imide)
PLA	poly(lactic acid)

PLD	pulsed laser deposition
PMMA	poly(methyl methacrylate)
ps	picosecond
PS	poly(styrene)
PTFE	poly(tetrafluoroethylene)
PTT	poly(trimethylene terephthalate)
SEM	scanning electron microscopy
SLIPS	slippery liquid infused porous surface
TEM	transmission electron microscopy
TTM	two-temperature model
UV	ultraviolet
VIS	visible
XPS	X-ray photoelectron spectroscopy

Chapter 1 Introduction

For solids, the surface layer dictates the way a material interacts with its surroundings. Thus, by modifying a material's surface, its properties can be altered. To that effect, several methods for material surface texturing have been developed such as milling, photolithography, and chemical etching. With the development of laser technology, laser machining emerged as an alternative texturing technique that offers several advantages. Indeed, it is a single-step, contactless method that can be used in any type of environment. Its operating principle relies on the absorption of focused laser pulses leading to selective material removal through ablation. Historically, its main limitations were the formation of a heat affected zone (HAZ) surrounding the ablated volume and its inability to machine transparent materials [1]. With the development of ultrashort laser pulses, both of these drawbacks have been mitigated [2]. The delivery of high energy pulses on a scale of femtoseconds (fs) can lead to the ablation of any type of material through non-linear absorption processes. In addition, the short timeframe of energy transfer limits the formation of the HAZ, thus enabling high quality machining of micrometric features. Furthermore, fs laser irradiation is typically accompanied by the formation of nanometric roughness atop of the machined area. The ability to create hierarchical structures that exhibit roughness on both microand nanometric length scales has led to the creation of materials with novel surface properties. For example, fs laser micromachining has been shown to produce both superhydrophobic [3] and superhydrophilic [4] behavior on both metallic and polymeric surfaces. Such surfaces have a very wide range of application including self-cleaning materials, microchannels for lab-on-chip devices, and biomedical materials for in-vivo use [5]. Therefore, studying the interactions of utlrashort laser pulses with matter became a research area of interest.

In the case of metallic surfaces, the different mechanisms that occur during ablation have been identified [6]. Furthermore, a photothermal model that describes the energy transfer taking place during the process has been developed [7]. However, polymeric surfaces have so far exhibited a different behavior. First of all, they are much more susceptible to photochemical reactions that change the composition at the surface [4, 8, 9]. Furthermore, they are more dependent on processing parameters such as pulse number (due to incubation effects) [10] and wavelength (due to nonlinear absorption) [8].

It has recently been shown that, under certain circumstances, novel porous structures with hierarchical roughness appear on fs textured poly(tetrafluoro ethylene) (PTFE) [3]. Such surfaces would be highly beneficial for applications were a large surface area is required such as catalysis and biomedical implant materials. For the latter, the combination of porosity and increased roughness can enhance cell attachment and growth on grafts, stents, and tissue engineering scaffolds [11, 12]. However, it is unknown if these structures can be reproduced on other polymers or under which operating conditions they appear. Due to the many non-linear optical processes and photochemical reactions involved, their optical and chemical surface properties are expected to differ from those of the non-modified polymer. Thus, a characterization of these properties would help elucidate the mechanisms at hand. One hypothesis is that these structures are related to the porosity observed on the bottom or side-walls of ablated lines and craters observed in previous publications [13-16]. These studies conjecture that pores appear as a consequence of homogeneous bubble formation during laser-induced explosive boiling. However, no experimental evidence has been put forth yet and the effect of viscoelastic melt properties which affect bubble formation has not been explored. Finally, the final properties of these structures are dictated by the material properties and machining procedure. Thus, even if the microstructure topology is optimized for a specific application, its surface properties such as wettability might be inadequate. Further tuning of these properties would require additional texturing of the surface which would compromise and overwrite the porous topology.

In summary, femtosecond laser micromachining of polymer surfaces can lead to the formation of novel structures with interesting topologies. A detailed investigation of their properties and formation mechanisms will thus facilitate their future optimization and implementation in real-life applications.

1.1 Objectives

The main objective of this thesis is to investigate, characterize, and optimize femtosecond laser-induced surface structures on polymer surfaces. The following specific objectives are addressed:

- i. Review of the state-of-the-art for femtosecond laser micromachining of polymers with emphasis on ongoing research.
- ii. Investigation of the favorable machining conditions and material-dependent

parameters for the formation of femtosecond-laser induced structures.

- iii. Optical and chemical characterization of femtosecond laser-induced structures and identification of the non-linear optical processes and photochemical processes at hand.
- iv. Presentation of experimental evidence of laser-induced explosive boiling and investigation of its dependence on viscoelastic melt properties.
- v. Development of a novel pulsed-laser-deposition process that allows the postmachining tuning of surface wettability without compromising the laser-induced topology.

1.2 Organization of the thesis

Chapter 2 is a yet to be published review chapter that is set to be included in a future handbook concerning laser micro/nano engineering. It presents the state-of-the art for femtosecond laser micromachining of polymers and contains all the technical background information required for the subsequent chapters. Chapter 3 is a conference proceedings article highlighting the laser-induced porous structures that form on several polymeric materials and identifies the conditions under which they appear. Chapters 4, 5, and 6 are original research articles published in peer-reviewed journals that address objectives iii, iv, and v respectively. They highlight the properties of femtosecond laser-induced porous structures and the formation mechanisms responsible for their unique topology. Novel approaches for the optimization of their dimensions and wettability are also presented. Finally, chapter 7 summarizes the main findings and original contributions to knowledge. A discussion of possible future research is also presented.

1.3 Contributions of authors

I designed and executed most of the experimental and analytical work presented in this thesis. Prof. Anne-Marie Kietzig supervised all of the work and edited all manuscripts. Mark Zhao contributed in the design, executed, and analyzed the experimental and analytical work related to the computed tomography results presented in chapter 5. Guillaume Forstmann contributed in the design, built, and tested the pulsed-laser-deposition setup presented in chapter 6.

Chapter 2 Laser Surface Structuring of Polymers and Functionalization

2.1 Preface

In this chapter, the state-of-the art for femtosecond laser micromachining of polymer surfaces is presented. First, a detailed explanation of the physical phenomena that govern polymer ablation is given. Then, the different structures that can be created using this technique are presented. Finally, the applications where these structures can be implemented are highlighted. Throughout the text, a strong emphasis on ongoing research in the field is made to highlight the current gaps in knowledge. This chapter will be published at a future time as part of the "Handbook of Laser Micro/Nano Engineering" (Springer). Thus, my contributions to the field are mentioned in the relevant sections even if they be will presented in greater detail in the following chapters.

Laser Surface Structuring of Polymers and Functionalization

Youssef Assaf, Anne-Marie Kietzig

In this chapter, a comprehensive review of femtosecond (fs) laser surface structuring of polymers and their subsequent functionalization is presented. First, the current state of knowledge concerning fs laser-polymer interaction is presented. The relevant non-linear optical phenomena and photochemical interactions that occur during processing are thus introduced. The discussion follows with an in-depth look at the novel laser-inscribed and laser-induced structures that this technique can currently impart on polymer surfaces. Several textures with hierarchical roughness such as trench arrays and porous networks are highlighted. Finally, the various ways in which these structures can be functionalized in order to target certain applications are described. This discussion includes wettability modification, microfluidic applications, optical applications, as well as biocompatibility enhancement.

Surface structuring, or the alteration of a surface's topology, is of utmost relevance in modern materials engineering. Indeed, novel materials are expected to be able to withstand increasingly harsh conditions or perform increasingly well under certain external conditions. Since a material's surface contains the outermost molecules that act as an interface with the surrounding environment, modifying its texture will have a significant impact on how it interacts with various media. This field has been historically limited by the minimum length scale of modification. Over the last few decades, several techniques that are able to successfully microtexture a surface such as etching, lithography, and laser machining have emerged. However, none of these have been able to successfully alter a surface's texture on the nano-scale. While photolithography has been able to recently achieve that, it remains a complex, multi-step process. With the advent of chirped pulse amplification, femtosecond laser pulses can now be readily generated. The development of such energetically concentrated pulses allows laser texturing to readily modify surfaces down to the nanoscale in a single processing step. Recent research in this area has led to an increased understanding of ultrashort laser interaction with metals which is typically governed by photon absorption by the surface electrons that subsequently diffuse into the bulk and interact with the surface phonons. As a consequence, a certain amount of material is removed through ionization leaving behind a textured surface. This has led to the development of hierarchically textured metals that are used in a wide variety of applications such as self-cleaning materials and water/ice-phobic

surfaces. However, femtosecond laser-polymer interactions are still under investigation as the nonlinear optical phenomena and photochemical reactions involved are not fully understood. This chapter will thus round up the current state of knowledge with regards to fs laser structuring of polymers and how applying it can lead to surface functionalization in order to target specific applications.

2.2 Polymer machining

As already mentioned, femtosecond laser interactions with polymers are governed by optical and chemical processes that are different than those for other materials. Thus, in this section, the non-linear optical processes and photochemical reactions that occur during femtosecond laser ablation of polymer surfaces will be discussed. In addition, current progress related to ongoing fundamental research being conducted in the field will be presented.

2.2.1 Ablation mechanisms

Laser texturing is a technique whose working principle lies in the energy delivery from incoming photons to a substrate's surface. Thus, for any specific material, the mechanism of photon absorption will play a major role in determining the machining outcome. For materials with high reflection, be it specular or diffuse, most incoming photons bounce off the surface. In addition, weakly absorbing materials will transmit and/or scatter most of the non-reflected photons. Most polymers either have very low absorption (i.e. poly(methyl methacrylate) (PMMA)) or are diffusely reflective (i.e. poly(tetrafluoroethylene) (PTFE)) with respect to visible light. This is why, without the use of additives, they generally appear either transparent or white. Their limited absorption is a direct consequence of their electronic structure. In order to better illustrate the uniqueness of polymer behavior, let us first consider photon absorption in conducting materials.

In metallic substrates, a large number of free electrons exist that can readily absorb incoming photons. Thus, the photon absorption rate is independent of light intensity and linear absorption is said to take place. Within a few femtoseconds, free electrons absorb the incoming photons and get heated to a temperature that is higher than that of the surrounding lattice [17]. Electrons then cool down by diffusing into the bulk and interacting with the lattice phonons. Depending on the incoming energy and the relevant material properties (thermal conductivity and electron-phonon coupling constant), this can lead to the ionization of a surface layer and material ablation. The two-temperature model (TTM), referring to the temperatures of the electrons and the lattice, is a mathematical model used to describe the heat transfer phenomena that occur during laser ablation of metals [7]. Thus, for conducting materials, the mechanisms of photon absorption and how it affects laser ablation is well understood.

In contrast, in polymer substrates, no free electrons are available due to covalent bonding. As a consequence, for laser ablation to take place, free electron generation through the excitation of valence band electrons to the conduction band has to occur. However, polymers typically have a large band gap whose energy is higher than that of an incoming photon. Single photon absorption is thus insufficient to generate free electrons. In this case, the only way to cross the band gap is to simultaneously absorb several photons through multiphoton absorption. Typically, the probability of multiple photons simultaneously colliding with an electron is too small for multiphoton absorption to occur. However, the high pulse intensity delivered by femtosecond laser systems has been shown to be sufficient to induce multiphoton absorption in dielectric materials such as polymers. However, it is not the only non-linear optical process that can lead to free electrons. At high enough intensities this can lead to a chain reaction of free electron generation termed as "avalanche ionization" [18]. Thus, the rate of increase of the free electron density n_e can be calculated by adding the contributions from both multiphoton and avalanche ionization:

$$\frac{\partial n_e}{\partial t} = \dot{n}_{mp} + \delta n_e \tag{1}$$

where \dot{n}_{mp} is the rate of multiphoton absorption and δ is the impact probability between a free electron and an atom. However, the application of equation 1 has led to contradicting results regarding its validity [19-23]. In her study, Rethfeld clarified these contradictions by modifying this model to better reflect the interactions between the two processes [24]. Indeed, for avalanche ionization to occur, not only do free electrons have to collide with atoms, they also need to have a high enough kinetic energy for the impact to create new free electrons. However, multiphoton ionization typically creates free electrons with a kinetic energy lower than that required for

avalanche ionization. Thus, free electrons generated by multiphoton ionization need to further absorb additional photons by intraband absorption in order to reach higher energy levels. By considering the rate of every absorption step, Rethfeld developed the multiple rate equation where equation 1 becomes:

$$\frac{\partial n_e}{\partial t} = \dot{n}_{mp} + \tilde{\delta} n_k \tag{2}$$

where δ is the impact probability of an atom with a free electron that has a kinetic energy that is high enough for avalanche ionization, and n_k is the electron density of free electrons with such high energy. Rethfeld then provided numerical results for a hypothetical scenario where SiO₂ is ablated with a laser with a photon energy of 2.48 eV. Her results showed that the relative contribution of each of the two processes depends on both the laser intensity and pulse duration. As seen in Figure 1, higher laser intensities promote avalanche ionization since it will lead to free electrons with higher kinetic energy. However, shorter pulse durations promote multiphoton ionization since energy is delivered on a timescale shorter than the one needed for sufficient intraband absorption to occur.



Figure 1: Percentiles (dashed lines) of free electrons generated by avalanche ionization with respect to total free electrons as a function of intensity and pulse duration. The characteristic time for avalanche ionization t_{MRE} (solid line) is also shown. Reproduced from [24].

After electron thermalization, temperature equilibration through electron diffusion and electron-phonon interactions takes place. For metals, the dynamics of electron-phonon coupling can be estimated by directly applying the TTM. For dielectrics such as polymers, the rapidly changing free electron density prevents the use of the same approach. A way of indirectly estimating the electron-phonon coupling constant e_{ph} is through the characteristic relaxation time of thermal equilibration τ_{relax} :

$$\tau_{relax} = \frac{c_e c_l}{(c_e + c_l)e_{ph}} \cong \frac{c_e}{e_{ph}}$$
(3)

where c_e and c_l are the specific heats of the electrons and lattice respectively. In his study, van Driel proposed a modified TTM model which takes into account rapidly changing free electron densities and through which τ_{relax} and e_{ph} can be estimated [25]. In their application of the model, Ramer et al. showed that, for femtosecond ablation of silicon, electron-phonon energy transfer is complete after almost 10 ps as seen in Figure 2 [26]. The modified TTM model also describes the diffusion of free electrons into the material bulk. However, due to the relatively low thermal conductivity of dielectrics, high spatial confinement of free carriers near the surface and large free carrier density gradients into the bulk are expected (electron diffusion depth on the order of 0.1 μ m for silicon).



Figure 2: Surface electron temperature T_e , phonon temperature T_{ph} , and free electron density n_e as a function of time for silicon with the duration of the laser pulse represented by the gray curve (arbitrary intensity). Reproduced from [26].

In summary, the heat transfer dynamics during femtosecond laser ablation of polymers is heavily dependent on their optical properties. The material band-gap acts as an obstacle to photon absorption, and free electron generation has to be induced through non-linear optical processes. After heat transfer from the electrons to the lattice occurs, phase changes that lead to material removal can take place. For any given material, if its surface is irradiated above a certain energy threshold, material removal through ablation will occur. This intrinsic property is termed as the threshold fluence F_{th} and is used in comparison to the incoming single pulse peak fluence F_0 :

$$F_0 = \frac{8E}{\pi\omega_0^2} \tag{4}$$

where *E* is the laser pulse energy and ω_0 is the beam spot diameter. Depending on the magnitude of F_0 , several ablation mechanisms have been reported as summarized in Figure 3.



Figure 3: Typical phenomena occurring during femtosecond laser irradiation of solids as a function of time and intensity. Reproduced from [27].

At moderate fluences, material removal through melting and vaporization occurs [6]. Both heterogeneous [28, 29] and homogeneous [30, 31] melt formation have been reported with homogeneous melting being more prevalent at higher fluences due to the higher energy requirement. The melting is often accompanied by other concurrent mechanical material removal mechanisms such as fragmentation and spallation [32]. Fragmentation is caused by the mechanical failure of the surface layer due to the stresses induced by the material expansion. On the other hand, pores can also develop near the material surface due to compressive stresses that arise as a

consequence of the impacting photon waves. These pores can grow and coalesce causing the top layer of the material to be shed off. This phenomenon is termed as spallation and is highlighted in Figure 4.



Figure 4: Simulation of the spallation of an arbitrary low-absorption material. Reproduced from [32].

While thermal melting can occur on any type of material, non-thermal melting can occur in dielectrics such as polymers at higher fluences. Indeed, if the excited electron cloud is heated fast enough, it can cause a lattice instability which causes the loss of solid lattice order on a timescale shorter than the time of lattice heating [33, 34].

As the melt layer gets heated further at higher fluences, it can cross the critical point causing new material removal phenomena to occur. At this point, massive homogeneous vapor bubble nucleation can occur causing material ejection in a phenomenon called explosive boiling or phase explosion [35]. At even higher fluences, heating above the critical point directly from the solid state and without the formation of liquid can occur [36]. This phenomenon leads to material decomposition and is called critical point phase separation. Finally, at sufficiently high fluences, the solid can be directly ionized into the plasma state. The mechanism of ionization is still under debate but, for dielectrics, the most accepted mechanism is Coulomb explosion [37]. In this case, outer valence electrons responsible for chemical bonding are stripped away from their atoms. The now non-bonded, positively charged atoms thus mutually repel each other and explode into a cloud of high velocity ions; hence generating a plasma.

While all of the phenomena discussed above occur at the material surface, it should be noted that femtosecond laser pulses can also be used to induce bulk modifications. Indeed, by focusing the incoming beam well below the surface of a transparent material, modification of bulk properties can be achieved while leaving the surface intact. This is particularly relevant for microphotonic applications and is described in greater detail in section 2.4.3.

In conclusion, several ablation mechanisms for solids irradiated with femtosecond lasers have been identified with a clear distinction between metallic and dielectric behavior. However, almost all of the abovementioned fundamental research on dielectric ablation has been performed on inorganic materials. While the behavior of polymers should be fundamentally similar due to their similar optical properties, the influence of their susceptibility to photochemical modification and of their macromolecular structure on ablation behavior is still relatively unexplored.

2.2.2 Effect of wavelength

As discussed in section 2.2.1, femtosecond laser ablation of polymers is strongly dependent on the optical properties of the substrate. The main barrier to free electron generation is the large optical bandgap, whose energy is typically larger than that of a single photon. However, that is only true for a certain wavelength range since photon energy E_p is directly related to wavelength λ :

$$E_p = \frac{hc}{\lambda} \tag{5}$$

where *h* is Planck's constant and *c* is the speed of light. Thus, at small enough wavelengths, photon energies are large enough so that single photon absorption is sufficient to cross the bandgap. This should have a significant impact on the ablation mechanism as multiphoton absorption is no longer required. This should theoretically improve the ablation efficiency and increase the ablation rate. Even if operating at small wavelengths such as ultra-violet (UV) radiation seems like a promising avenue to explore for process optimization, very few publications have studied the topic. Currently, the solid state or fiber lasers that are used for material processing research all emit beams in the near infrared (IR) (750-1400 nm) [38]. Thus, femtosecond laser radiation with lower wavelengths can only be produced by additional harmonic generation or parametric amplification. This could explain the scarcity of publications dedicated to the study of the effect of wavelength on dielectric and polymer ablation.

One of the few such publications is Okoshi et al's study on the femtosecond laser ablation of poly(ethylene) (PE) [8]. In their experiments, polyethylene was ablated at two wavelengths: 790 nm and its second harmonic (395 nm). They observed that, for the same fluence, the etching depth was higher at 395 nm (Figure 5). However, operating at the shorter wavelength also induced chemical modification in the form of isolated carbon, C=O, and C=C-H bonds. They then mixed a faint 395 nm beam (2.5% of total fluence) into the 790 nm beam and noticed that it resulted in an even higher etching depth with limited chemical modification. While their study did not relate these results to the bandgap structure of the material, it did show that wavelength is an important operating parameter that can be used to optimize femtosecond laser ablation of polymers.



Figure 5: Comparison of etching depth versus fluence between a) 395 nm (triangles) and 790 nm (circles) and b) 790 nm (circles) and a mixture of 395 nm (2.5%) and 790 nm (97.5%). Reproduced from [8].

More recently, Hernandez-Rueda et al. have ablated waveguides on fused silica using five different wavelengths produced by optical parametric amplification ranging from 400 nm to 1300 nm [39]. Their results suggest a decrease in the modification threshold at shorter wavelengths. In addition, their numerical simulation suggests that the contribution of avalanche ionization is significantly reduced at longer wavelengths.

Finally, in a recent publication, Assaf et al. have characterized the optical and chemical properties of polymer surfaces machined at two distinct wavelengths (λ =800 nm and λ =275 nm) [40]. They have observed that polymer behavior depends on its cut-off wavelength λ_c , below which the energy of a single photon is larger than the bandgap energy. Below λ_c , low single pulse threshold fluences and high linear absorption coefficients were measured. Above λ_c , high threshold fluences were measured and multiphoton absorption was determined to be taking place. These distinct absorption behaviors also affected the ablated structures as significantly more melt was observed at λ =275 nm relatively to λ =800 nm.

In conclusion, the few studies concerning the effect of wavelength on the ablation behavior of dielectrics and polymers suggest that it strongly affects ablation efficiency and can affect surface chemistry. The known photochemical processes that have been reported to occur during femtosecond laser machining of polymers are presented in the following section.

2.2.3 Effect of substrate chemistry

One of the properties of polymers that distinguishes them from other materials is their susceptibility to chemical modification during laser machining. Even before the advent of femtosecond laser technology, polymers have been observed to undergo photochemical reactions upon laser irradiation. Dyer et al. observed that, after etching poly(ethylene terephthalate) (PET) with a nanosecond laser, volatile products such as carbon monoxide, carbon dioxide, and methane were being produced [41]. Their subsequent analysis determined that the gas and other non-volatile ablation products were a result of thermal decomposition. Similarly, Srinivasan et al. observed the decomposition of poly(imide) (PI) into volatile decomposition products such as carbon monoxide, ethane, hydrogen cyanide, and carbon dioxide during laser ablation [42]. Lippert et al. later made similar observations on the nanosecond laser ablation of triazene polymers [43] and PMMA [44] where benzene and methyl methacrylate gas were detected during machining respectively. Thus, for polymers, the high temperatures achieved during machining lead to the fragmentation of the macromolecular chains into smaller decomposition products.

More recently, concurrent with the development of femtosecond laser technology, the focus has shifted from analyzing the ablation products to chemically characterizing the laser modified surface. For example, in their studies of the laser ablation of PE, Okoshi et al. have detected the increase in C=O bonds after machining by Fourier transform infrared spectroscopy [8, 45]. Similarly, Wang et al. have reported the increase of polar functional groups such as C=O bonds on the surface of PMMA after laser irradiation, which caused an increase in surface hydrophilicity [4]. They attributed this change in surface chemistry to photodegradation. More recently, Yada et al. have also observed the increase of carbon-oxygen peaks on poly(lactic acid) (PLA) after machining by X-ray photoelectron spectroscopy [9]. In summary, femtosecond laser micromachining of polymer surfaces can lead to the increportation of oxygen into the surface.

While several other publications report similar results [46-48], some contradiction still exists in the literature. For example, De Marco et al. [49] and Jia et al. [50] reported no laserinduced chemical modification on PMMA and PLA respectively. Furthermore, Pazokian et al. [51] observed an increase of surface carbon at the expense of oxygen on poly(ether sulfone) (PES). These diverging results are a result of most publications being interested in the ablation of a specific polymer at specific conditions. In a recent publication, Assaf et al. performed a comparative study where six different polymers were machined at two different wavelengths and at several fluences [40]. An increase in surface oxygen was observed for PE, poly(carbonate) (PC), PET, and, to a lesser extent, PTFE due to photo-oxidative mechanisms. This effect was more pronounced for UV irradiation when compared to near-IR irradiation. In contrast, no change in surface chemistry was observed on PMMA and PLA which the authors attributed to their resistance to photo-oxidation.

In conclusion, femtosecond laser micromachining of polymers can alter the surface composition. This can affect machining behavior through incubation effects as will be discussed in the following section.
2.2.4 Effect of pulse number

Incubation effects are a phenomenon by which increasing the number of incoming pulses on a surface will lower its threshold fluence. They can be mathematically described by the model developed by Jee et al [52]:

$$F_{th}(N) = F_{th}(1)N^{\xi - 1} \tag{6}$$

where $F_{th}(1)$ is the single pulse threshold fluence, $F_{th}(N)$ is the threshold fluence after a certain number of pulses *N*, and ξ is a material-dependent incubation coefficient. Polymers are typically more susceptible to incubation effects than other materials as many publications have reported their occurrence [13, 14, 53-56]. However, incubation remains an empirically observed and quantified parameter, and the physical origin behind it remains uncertain. So far two main hypotheses have been put forth. In their study of PMMA laser ablation, Kuper et al. first suggested that incubation is a consequence of a local increase in absorption [57, 58]. They state that, as more and more pulses are delivered to the surface, light transmission is decreased and energy accumulation happens closer to the surface, thus resulting in an increased absorption and decreased threshold fluence. Similar observations were made on dielectric materials. For example, Lenzner et al. observed a four-fold decrease in ablation threshold for fused silica when irradiating the sample with 50 pulses as opposed to a single pulse [59]. While a few publications briefly mention a change in color resulting from laser irradiation of polymers [8, 60], no effort has been made to relate it to the increase in absorption.

So far, two main approaches to relate the incubation behavior to actual physical properties have been proposed. The first approach, proposed by Kim et al., is the heat accumulation model [61]. When a laser beam irradiates the surface, its energy is ultimately converted into heat. At high repetition rates such as the ones observed in femtosecond laser micromachining, significant heat accumulation can occur. Thus, the energy required for material ablation decreases. The heat accumulation is described by the following equation:

$$F_{th}(N) = T_c \frac{c_h t_h}{\beta} \frac{8\delta_T}{(\frac{\omega_0}{2})^2 f_p} \frac{1}{2} \ln^{-1} \left(\frac{8\delta_T}{\omega_0^2} \frac{N}{f_p}\right)$$
(7)

where T_c is the critical temperature required for material ablation, c_h is the volumetric heat capacity, t_h is the thickness of the sample, β is the portion of incident light that is absorbed, δ_T is

the thermal diffusivity, and f_p is the repetition rate. This model breaks down at large spot sizes and leads to non-physical behavior. Indeed, if the logarithmic term is smaller than unity, then threshold fluence increases with pulse number, which contradicts experimental observations. The second approach is based on DeShazer et al.'s defect model [62]. This model assumes that any surface is covered by randomly distributed defects that locally enhance the optical field and thus have a lower threshold fluence F_d . The probability Π of irradiating at least one defect with a fluence larger than F_d is given by:

$$\Pi = 1 - \left(\frac{F_0}{F_d}\right)^{-\frac{\omega_0^2 \pi \sigma}{2}} \tag{8}$$

where σ is the spatial density of defects. Thus, an expression of F_{th} as a function of F_d and the threshold of the defect-free material F_i can be obtained:

$$F_{th} = F_d + (F_i - F_d) \left(\frac{F_i}{F_d}\right)^{-\frac{\omega_0^2 \pi \sigma}{2}}$$
(9)

Naghilou et al. extended this defect model to include the effect of multiple pulses by attributing incubation coefficients ξ_d and ξ_i to the surface defects and the defect-free surface respectively [63]. They thus ended up with an expression for the overall incubation coefficient ξ which was in good agreement with their experimental results on high impact poly(styrene) (PS):

$$\xi = \xi_d + (\xi_i - \xi_d) \frac{\frac{F_i(1)}{F_d(1)} - \frac{1}{2}\omega_0^2 \pi \sigma(\frac{F_i(1)}{F_d(1)} - 1)}{\frac{F_i(1)}{F_d(1)} + \left(\frac{F_i(1)}{F_d(1)}\right)^{-\frac{1}{2}\omega_0^2 \pi \sigma} - 1}$$
(10)

The physical nature of the defects themselves is still under debate. Genin et al. [64], as well as Smith et al. [65], argue that any crack or roughness valley in the surface will locally enhance the optical field by promoting reflection and scattering. Other authors mention that defects are induced by the accumulation of conduction band electrons for transparent materials [66-68] or enhanced energy coupling efficiency due to laser induced surface plasmons for metals [69].

While all of the abovementioned publications discuss physical surface defects, Baudach et al. suggest that substrate chemistry plays a large role in incubation behavior [70]. They measured the threshold fluence of six different polymers at six different pulse numbers and fitted the data to equation 6 in order to obtain the incubation coefficient ξ (Table 1).

		F_{th} (J/cm ²))		
	<i>N</i> =1	<i>N</i> =5	<i>N</i> =10	<i>N</i> =100	ξ
PI	1.0	0.8	0.7	0.5	0.87
c-PET	1.8	1.5	1.0	0.3	0.60
a-PET	2.1	1.5	1.0	0.4	0.63
PC	1.8	1.4	1.2	0.5	0.73
PTFE	1.9	1.4	1.2	0.7	0.78
PMMA	2.6	2.3	1.5	0.6	0.67

Table 1: Threshold fluence as a function of pulse number and incubation coefficients for different polymers. Prefixes a- and c-stand for amorphous and crystalline respectively. Reproduced from [70].

Among the studied polymers, PC, PET, and PMMA were the most affected by incubation effects as reflected in their low values of ξ . In contrast, PI and PTFE were less affected and displayed large incubation coefficients. The authors argued that the ester bonds in PC, PET, and PMMA are much less stable than the inert PI and PTFE bonds. Thus, ester bonds experience preferential bond breaking during ablation and significantly contribute to incubation effects. However, no chemical data was presented alongside these results in order to check for evidence of preferential ester bond breaking.

Finally, the recent work by Assaf et al. on the characterization of femtosecond laser machined polymer surfaces highlights both the optical and chemical contributions to incubation effects [40]. As discussed in section 2.2.2, the authors observed that, for single pulse ablation, polymers absorb wavelengths that are longer than their cut-off value λ_c through multiphoton absorption. However, they observe a shift towards linear absorption at higher pulse numbers. Thus, as more and more pulses are applied to the surface, the optical properties of a polymer change and its absorption increases. This was validated by spectroscopy measurements and was even visible by eye as all studied polymers displayed a loss of transparency after machining. This change in optical properties was measured to be a major contributor to incubation effects as much lower incubation coefficients were measured when machining above λ_c . Furthermore, some polymers experienced photo-oxidation as discussed in section 2.2.3. These polymers displayed an increasingly darker color as machining fluence increased due to an increase in surface oxygen. For

these materials, the incubation coefficient was lower than for non-reactive materials, thus highlighting the chemical contribution to incubation effects.

In conclusion, femtosecond laser micromachining of polymers is a process that is very sensitive to pulse number due to incubation effects. Several factors have been shown to contribute to incubation such as heat accumulation, changes in optical properties, accumulation of surface defects, and preferential bond breaking. All of these processes occur simultaneously and a quantitative model that separates the contribution of each phenomenon has yet to be developed.

2.3 Surface texturing

In the previous section, the fundamentals behind femtosecond laser-polymer interaction have been presented. The end-result of these interactions is the removal of material through ablation, thus resulting in a textured surface. In this section, the different microstructures that can be produced on polymers by femtosecond laser machining will be presented. Both laser-inscribed and laser-induced structures will be discussed.

2.3.1 Laser-inscribed structures

When a surface is ablated by a laser pulse, a certain geometry will be inscribed into the surface due to the removal of a certain volume of material. If operating with a circular beam and a stationary setup, the inscribed geometry will be that of a circular hole. However, if either the beam or the sample are translated with a velocity that allows for consecutive pulses to significantly overlap, then a line can be inscribed into the surface. Figure 6 is a graphical representation of a typical line inscription with the equation relating the distance between two consecutive pulses Δx with the scanning velocity v and repetition rate f_p highlighted.



Figure 6: Laser line inscription

Since consecutive pulses do not fall atop one another, the average pulse-per-spot number *PPS* has to be calculated from processing parameters:

$$PPS = \frac{\omega_0 f_p}{v} \tag{11}$$

For this type of machining, the two main design parameters are the ablated width D, and the ablated depth-per-pulse d, so as to inscribe holes or channels with the desired dimensions. Typical laser inscribed geometries are shown in Figure 7.



Figure 7: Examples of laser-inscribed geometries on polymer surfaces: a) microchannels inscribed on PMMA [71] and b) hole array inscribed on poly(dimethyl siloxane) (PDMS) [72].

Liu derived a model that relates ablated width *D* to the peak pulse fluence F_0 , the material threshold fluence F_{th} , and the beam spot diameter ω_0 for a Gaussian beam [73]:

$$D^{2} = \frac{1}{2}\omega_{0}^{2}\ln(\frac{F_{0}}{F_{th}})$$
(12)

This relationship was derived by considering the spatial profile of the beam spot and the threshold fluence of the material. As already mentioned, a material will only get ablated if it receives a fluence higher than its threshold value. And since a Gaussian beam's intensity continuously decreases away from its center, only a portion of the beam spot can be located above the threshold fluence as can be seen in Figure 8. Furthermore, as the fluence increases, a larger portion of the beam will have an intensity that is above the threshold. By equating the ablated width to the width of the beam at the threshold and solving for D, equation 12 is obtained. By constructing a semilogarithmic plot of the squared ablated width versus fluence, the threshold fluence and spot size can be estimated.



Figure 8: Effect of threshold fluence on ablated diameter. Reproduced from [10].

In several publications regarding femtosecond laser ablation of polymers, line width [3, 74-77], or hole diameter [16, 78] was observed to increase with increasing fluence until reaching a certain maximum value as described by Equation 12. Also, in some cases, using high fluence values was reported to be detrimental to machining quality since it resulted in increased debris deposition [74]. In summary, ablated line width on polymers is relatively simple to predict by simply applying Liu's model.

While the dependence of ablation width on fluence depends mostly on the incoming beam, that of the ablation depth depends on the optical properties of the material itself. For linearly absorbing materials, the fluence decays as a function of the depth into the surface z according to the absorption coefficient α :

$$F(z) = F_0 e^{-\alpha z} \tag{13}$$

Similarly to the analysis for ablated width, material will only get ablated while the fluence is still above the threshold value. In other words, the depth of the ablated geometry will be equal to the distance between the surface and the point where light intensity equals the threshold value. Solving for *d*, the following expression is obtained:

$$d = \frac{1}{\alpha} \ln(\frac{F_0}{F_{th}}) \tag{14}$$

Threshold fluence and the absorption coefficient can therefore be estimated from a semilogarithmic plot of depth-per-pulse versus fluence. In summary, for linearly absorbing materials, knowing the material dependent threshold fluence and absorption coefficient is sufficient to estimate line width and depth. However, as explained in section 2.2.1, polymers absorb incoming photons through non-linear optical processes. Depending on the bandgap energy, electrons have to simultaneously absorb a minimum number *m* of electrons in order to get excited into the conduction band. Preuss et al. stipulated that, for dielectric materials, any absorption of the order less than *m* can be ignored and the decay of light intensity *I* into the material is governed by the *m*th order absorption coefficient α_m [79]:

$$\frac{dI(z)}{dz} = -\alpha_m I^m \tag{15}$$

Recently, Grehn et al. have adapted Preuss et al.'s work to the femtosecond laser ablation of dielectrics by a Gaussian beam with pulse duration τ and obtained the following relationship for d [80]:

$$d = \frac{\tau^{m-1}}{(m-1)\alpha_m} \left(\frac{1}{F_{th}^{m-1}} - \frac{1}{F_0^{m-1}} \right)$$
(16)

In their study, the depth data obtained on Borofloat glass and $LiGe_{50}Si_{25}$ were in excellent agreement with this model. While this model should apply to most materials that undergo multiphoton absorption processes, some authors reported that depth versus fluence data for most dielectrics follow a trend that is closer to that of metals [10, 81-83]:

$$d = \frac{1}{\alpha_{eff}} \ln(\frac{F_0}{F_{th}}) \tag{17}$$

where α_{eff} stands for the effective absorption coefficient that takes into account non-linear effects and is typically larger than the linear absorption coefficient α . In summary, determining ablation dimensions remains empirical and cannot be accurately predicted from optical properties alone as many optical phenomena can occur depending on material properties and machining conditions.

Finally, one thing to note about femtosecond laser-inscribed structures is that, even if the microscale topology is imposed by the scanning procedure, the surface of the ablated material is in some cases covered by a random nanoscale texture as can be seen in Figure 9.



Figure 9 : a) Square array microchannel pattern on PDMS and b) high magnification image of the nanostructure found at the bottom of the microchannels [84].

The mechanisms behind the formation of the nano-roughness have been extensively studied with nanoparticle re-deposition and nanoscale melt being identified as the main hydrodynamic processes responsible [85]. The ability to create roughness on both the micro- and nano- scales in a single processing step is one of the main advantages of femtosecond laser micromachining. This allows the design of novel materials for advanced applications as will be discussed in section 2.4. In summary femtosecond laser micromachining of inscribed structures is inevitably accompanied by laser-induced structures on the surface of the ablated material. The next section will present the main laser-induced structures observed on polymeric substrates.

2.3.2 Laser-induced structures

As introduced in the previous section, the geometry of laser-inscribed structures is imposed on the surface by the machining trajectory, and their dimensions are typically on the scale of the laser spot diameter. In contrast, laser-induced structures are typically smaller than the spot diameter and form due to the reorganization of the surface layer as a response to laser irradiation. For polymeric substrates, two main types of femtosecond laser-induced structures have been reported so far: laser-induced periodic surfaces structures (LIPSS) and laser-induced porosity.

LIPSS formation on a polymer surface by femtosecond laser micromachining was first reported by Heitz et al. in their study of the ablation of PI [86]. Baudach et al. later produced the same structures and observed that their orientation was dependent on light polarization as can be seen in Figure 10 [87].



Figure 10: Ablation on PI with linearly polarized light (a-b) and circularly polarized light (c-d). Reproduced from [87].

Irradiation with linearly polarized light led to the formation of periodic nanoripples with a period comparable to the laser wavelength (800 nm). By rotating the sample at different angles and repeating the experiment, the LIPSS were observed to be always parallel to the light polarization. Forster et al. reported the formation of LIPSS with similar properties on PI and observed that their formation is more likely at short pulse durations and high frequencies [83]. LIPSS that have dimensions on the order of the incoming wavelength have been observed on many different types of solid surfaces, especially metals, for fluences close to the ablation threshold [88]. Their formation is thought to be caused by the interference between the incident laser beam and a scattered optical wave at the surface [89]. The periodicity Λ of the LIPSS therefore depends on the polarization, wavelength λ , and incident angle θ . For example, for p-polarized light:

$$\Lambda = \frac{\lambda}{1 \pm \sin\theta} \tag{18}$$

Figure 10c and 10d show that, upon irradiation with circularly polarized light, the LIPSS have a conical morphology and have a radial orientation. The authors were unsure regarding the cause of this change in shape but suggest that it might be due to shielding and diffraction effects induced by impurities in the sample.

In a later study, Rebollar et al. have shown that the periodicity and the amplitude of femtosecond LIPSS on polymer surfaces can be manipulated through the machining parameters. They demonstrated that, at fluences slightly below the ablation threshold, periodic nanoripples that are parallel to the incoming light polarization can be obtained on PC, PET, and poly(trimethylene terephthalate) (PTT) under both UV (λ =295 nm) and near-IR (λ =795 nm) irradiation [53, 90]. They measured the period and height of the nanoripples at both wavelengths and different fluences and pulse numbers. Figure 11 presents their results on PET.



Figure 11: Effect of fluence, pulse number, and wavelength on the period and height of LIPSS on PET. Reproduced from [53].

Both the period and the height were observed to increase with fluence until reaching a plateau value which, in the case of the period, is equal to the laser wavelength. The same behavior

was observed for the dependence on the number of pulses. Larger pulse numbers and fluence values were required to induce LIPSS formation in the near-IR when compared to the UV due to the lower absorption at this wavelength. In addition, the ripple heights achieved at 795 nm were overall slightly higher than those achieved at 295 nm. Atomic force microscopy (AFM) measurements showed that ripples had peaks and valleys which are respectively above and below the original surface position. Since these ripples were formed below ablation threshold, this suggests that the LIPSS were formed simply due to material rearrangement without the occurrence of ablation. Thus, the authors argue that the more efficient absorption at 295 nm confines the energy absorption and material rearrangement to the first few outer layers, resulting in slightly smaller ripple heights.

Finally, all of the abovementioned studies report that the ripples are parallel to light polarization. In contrast, LIPSS formed on metallic surfaces are widely reported to be perpendicular to polarization [88, 91]. This discrepancy remains unexplored and a mechanism explaining the reason behind it has not been put forth yet.

Another surface structure of interest on polymers is femtosecond laser-induced porosity. It was first reported by Baudach et al. in their study on the ablation of PC and PMMA [15]. By inscribing circular holes onto the surfaces with a single pulse, they observed surface swelling accompanied by pore formation. At higher pulse numbers, material ablation took place leaving behind a roughened porous texture at the bottom and side walls of the ablated crater. Later studies by Kruger et al. [14], Guay et al [13], and Baset et al. [16] reported the appearance of a similar structure on the bottom or side walls of ablated holes and lines on PMMA. Some of the structures reported by these authors are presented in Figure 12.



Figure 12: Femtosecond laser-induced porosity on: a) PC and b-d) PMMA. Reproduced from [15], [14], [13], and [16] respectively.

Baudach et al. suggest that surface swelling is due to melting and fractionation of CO-O bonds leading to the formation of gaseous products such as carbon dioxide. This causes the localized bursting of the surface and ejection of the melt. The same argument was put forth by Kruger et al.. Guay et al. put forth a similar explanation as they state that porosity is induced by explosive boiling. This phenomenon, also termed as phase explosion, is specific to femtosecond laser ablation. The shortness of the timescale of energy transfer to the surface (within the first few picoseconds [92]) leads to near isochoric volume heating and rapid adiabatic expansion. If a certain critical temperature is surpassed, then massive homogeneous nucleation of vapor bubbles can occur [93]. The two-phase liquid-gas system then undergoes hydrodynamic expansion resulting in material ejection. The melt then re-solidifies within a duration on the scale of nanoseconds, thus resulting in pore formation. In their study, Guay et al. performed numerical simulations of the ablation process on PMMA that suggested a volume heating up to 10^3 K, thus confirming the possibility of explosive boiling. Baset et al. suggested that the same mechanism is responsible for porosity formation but also studied the effect of processing parameters on pore size by performing image analysis on ablated craters. They observed that the porous area fraction decreases with increasing pulse energy for hole ablation and increasing scanning speed for line ablation. They also remarked that higher pulse energies lead to a decrease in pore size and increase in pulse

number. However, no physical explanation relating these results to processing parameters was given.

While the above discussion focused on laser-induced structures at the surface of laserinscribed structures, laser-induced structures can also be homogeneously produced over an entire surface by raster scanning (Figure 13). For this type of machining, lines are inscribed in one direction and overlapped in the other. The distance between two consecutive lines Δz is related to the beam spot diameter ω_0 and the overlap percentage desired between two consecutive lines Φ . In this case, the average pulse-per-spot number *PPS* is calculated in a slightly different manner:



Figure 13: Raster scanning.

Liang et al. reported that raster scanning PTFE leads to the formation of a porous hierarchical structure as seen in Figure 14 [3]. The structure was produced by machining at high overlap in order to ensure homogeneous structure formation. Very recently, Assaf et al. have reported the formation of similar porous structures on PC, PE, PET, PLA, PMMA and PTFE that was dependent on operating fluence and was accompanied by a change in optical properties (Figure 15) [40, 94]. They observed that porous structure formation is more prevalent for materials with a high threshold fluence at operating conditions. This can be explained by considering an explosive

boiling mechanism. For polymers with a low threshold fluence, most of the incoming energy is converted into material ionization and the underlying melt layer is heated to moderate temperatures. For materials with a high threshold fluence, the majority of the incoming energy profile is below the ionization threshold. Thus, the underlying melt layer is heated to much higher temperatures and can surpass the critical temperature for explosive boiling. At these conditions, massive homogeneous bubble formation occurs. However, this melt layer is rapidly quenched to room temperature in between laser pulses leaving behind pores that correspond to the volume occupied by bubbles during explosive boiling. Yong et al. later reproduced similar structures on most of the same polymers with the addition of poly(amide) (PA) [95, 96].



Figure 14: Homogeneous laser-induced porous microstructure on poly(tetrafluoroethylene) at different magnifications. Reproduced from [3].



Figure 15: Laser induced porous structures at different fluences. All scale bars represent 4 μ m. Inset is a 3 \times 3 mm photograph of the sample placed on white paper on which letters were printed to highlight the change in color and transparency. Reproduced from [40].

In conclusion, femtosecond laser micromachining can lead to the formation of novel laserinduced microstructures. Their unique morphology renders them prime candidates for many applications as will be discussed in section 2.4.

2.4 Applications

In the previous section, the various microstructures that can be imparted onto a polymer surface by femtosecond laser micromachining have been presented. These microstructures present unique morphological properties such as a multiscale roughness. These properties make them relevant for many applications which will be presented in this section.

2.4.1 Tunable wettability

Femtosecond laser micromachining has been demonstrated to be an effective tool for the modification of polymer surface wettability due to the multi-scale roughness it produces (section 2.3). Such structures can exhibit extreme wetting behaviors such as superhydrophilicity and superhydrophobicity. For a superhydrophilic material, a droplet will fully spread on its surface. On the other hand, if it the droplet exhibits a contact angle larger than 150°, the material is said to be superhydrophobic. The other requirement for superhydrophobicity is that the droplet should roll off as soon as the surface is slightly tilted (maximum sliding angle of 10°).

Rough surfaces, such as the ones produced by laser micromachining, can be modeled as containing a series of protrusions separated by asperities. Depending on many factors such as the nature of the solid, nature of the liquid, and protrusion geometry, a liquid droplet can either completely or partially penetrate into these asperities (Figure 16). The former case is termed as Wenzel wetting [97] (Figure 16a) while the latter is termed as Cassie-Baxter wetting [98] (Figure 16b). In the Cassie-Baxter state, the water droplet is sitting on air pockets that are trapped in the roughness asperities of the solid. The surface area between the liquid and the solid is therefore much less than for the Wenzel wetting state, and higher contact angles as well as lower sliding angles can be achieved.



Figure 16: a) Wenzel and b) Cassie-Baxter wetting states on rough surfaces.

Superhydrophobicity can only be achieved through the Cassie-Baxter wetting state. Researchers have arrived at this conclusion by observing naturally-occurring superhydrophobic surfaces such as the lotus leaf. Three general types of surface structures that can achieve Cassie-Baxter wetting were identified as illustrated in Figure 17: nanostructured, microstructured, and hierarchically structured [99]. Even though some superhydrophobic plant leaves observed in nature have a unitary structure (only nano- or micro-structured), the majority preferentially show hierarchical structures since the increased roughness enhances air-trapping. Thus, the creation of hierarchical structures with multi-scale roughness has become a design objective to obtain superhydrophobic behavior in synthetic surfaces. As presented in section 2.3, femtosecond laser micromachining is an excellent tool for the single-step formation of hierarchical roughness on polymer surfaces (Figures 9, 14, and 15). This is why it has been extensively used as a research tool for the wettability modification of polymers.



Figure 17: Types of surface structures that can exhibit Cassie-Baxter wetting. Reproduced from [99].

The first report of the creation of a superhydrophobic polymeric surface by femtosecond laser micromachining was reported in Yoon et al.'s study on PDMS [100]. As can be seen in Figure 18a, a high surface area hierarchical structure was obtained by raster scanning the sample surface. The roughness ratio of the observed structure was estimated by processing images obtained by atomic force microscopy. It was observed to increase with increasing fluence up to a value around

2.5. Consequentially, the contact angle was observed to increase from a value of around 100° up to a value around 175°. In addition, while droplets strongly adhered to the non-modified surface at any angle, the sliding angle was observed to decrease with fluence down to a value close to 2°, thus rendering the surface effectively superhydrophobic. In a more recent study, Yong et al. textured a PDMS surface with patches of the superhydrophobic structure (Figure 18b) organized in different 3D patterns [101]. By ablating different geometries, they created high contact angle surfaces (all above 150°) with varying adhesion displaying sliding angles as low as 1° and up to more than 90°. They attribute this tunable adhesion to the different wetting, or a number of metastable states where the droplet partially penetrates into the roughness features.



Figure 18: Superhydrophobic structures created on PDMS with inset photographs of a sessile drop sitting atop the surface with contact angles: a) 166° and b) 157°. Reproduced from [100] (a), and [101] (b).

Another polymer that was reported to behave similarly is PTFE. Due to its low surface energy, it is typically hydrophobic even prior to surface modification. This is why several authors have attempted to texture it by femtosecond laser micromachining in order to induce superhydrophobicity. As discussed in section 2.3.2, Liang et al. have created a homogeneous hierarchical porous structure on PTFE by raster scanning the sample surface (Figure 14) [3]. This structure increased the contact angle of the surface from 107° to 151°. Its superhydrophobic behavior was further highlighted by filming a falling droplet impact on the surface (2 mm diameter, 5 cm drop height). As can be seen in Figure 19, the droplet did not wet the surface whatsoever but rather performed a complete rebound thus highlighting the robustness of the surface superhydrophobicity. The structure also exhibited an oleophobic behavior as it displayed large

contact angles for several low surface tension liquids such as glycerol (135°), ethylene glycol (133°), and propylene glycol (124°). In a later study, Toosi et al. created similar structures on PTFE by biaxially ablating trenches into the surface [102]. By manipulating the channel height and morphology by varying operating fluence and overlap, they managed to obtain superhydrophobic surfaces with contact angles up to 170°.



Figure 19: Rebounding droplet on a superhydrophobic PTFE surface. Reproduced from [3].

Femtosecond laser micromachining does not only induce hydrophobicity. In their study on the laser ablation of poly(methyl methacrylate), Wang et al. reported that, depending on the magnitude of the applied fluence, either hydrophilicity or hydrophobicity is induced [4, 103]. As can be seen in Figure 20, the non-modified PMMA displayed a mildly hydrophilic contact angle of 75°. As soon as the ablation threshold is reached, the contact angle rises to 125°, thus rendering the surface hydrophobic. Further increasing the fluence gradually decreases the contact angle until a droplet completely spreads on the surface, effectively making the surface superhydrophilic. This behavior was explained by chemically analyzing the surface at each fluence by X-ray photoelectron spectroscopy (XPS). For low fluence values where the surface was hydrophobic, an increase of non-polar C-C bonds was observed. On the other hand, for high fluences, an increase in polar O=C bonds was observed, thus explaining the increase in hydrophilicity. The authors attributed these results to photodegradation, but no explanation for the discrepancy between low fluence and high fluence results was given. Pazokian et al. presented inverse results on PES where the originally hydrophilic material experienced an increase in hydrophilicity at low fluences and an increase in hydrophobicity at high fluence [51]. Furthermore, De Marco et al's extensive study on the properties of femtosecond laser micromachined PMMA gave results that are in contradiction with those of Wang et al.'s [49]. In their study, the contact angle was observed to switch from hydrophilic to hydrophobic at all fluence values above threshold. Furthermore, their XPS analysis did not show any increase in polar group formation. In contrast to Wang et al's study,

they attributed the wetting behavior of machined PMMA to the increased roughness that results in a metastable Cassie-Baxter wetting state with partial penetration into the roughness grooves. A similar contradiction exists for PS with different studies reporting either an increase in hydrophilicity [104] or hydrophobicity [105] attributed to surface chemistry or surface roughness respectively. In summary, despite the few contradictions in literature, these results show that surface chemistry can play as important of a role as surface roughness, when it comes to tuning the wettability of polymer surfaces by femtosecond laser micromachining.



Figure 20: Effect of fluence on the contact angle of laser modified PMMA. Reproduced from [103].

In conclusion, femtosecond laser micromachining of polymer surfaces can induce a wide array of wettabilities ranging from superhydrophilic to superhydrophobic behavior. Such surfaces, which exhibit extreme wetting behavior, have a very wide range of application including selfcleaning materials, microchannels for lab-on-chip devices, and biomedical materials for in-vivo use as will be discussed in the following sections.

2.4.2 Microfluidic applications

In recent years, there has been a growing interest for the development of miniaturized labon-chip devices. They offer many advantages for clinical and analytical laboratory analyses including increased sensitivity, decreased analysis time, and decreased analyte and reagent volumes. One of the major components of lab-on-chip devices are microfluidic channels used to transport fluids between the different chip compartments. Femtosecond laser micromachining can be used for the inscription of micrometric channels with limited thermal damage and micrometric resolution as described in section 2.3.1. Furthermore, it can induce hierarchical structures on the channel walls that can alter the surface's wetting properties as described in section 2.4.1. This is why its application to the fabrication of microfluidic channels for lab-on-chip devices is currently being studied.

One of the first publications on this topic is Day et al.'s study of the ablation of microchannels in PMMA in a water environment [106]. After inscribing lines with widths going down to 8 µm, they observed spontaneous water intrusion into the channels by capillary action. Zheng et al. inscribed similar microchannels into PC and argued that they would be suitable for use in an optical bubble switch where the channel would house an air bubble and a refractive-index-matching fluid [107]. Then, based on thermocapillary action actuated by microheaters, the bubble can block the junction of two waveguides, thus switching the optical signal path. The fabrication of high-quality microfluidic channels on several other polymers such as ethylene glycol dimethacrylate (EGDMA), PS, and cyclic olefin polymer (COP) was later demonstrated by Lim et al. [108] and Suriano et al. [109].

Wang et al. were the first to exploit fs-laser induced wettability changes in the design of microchannels [103]. In their study, they machined a microchannel on PMMA that splits into two following a Y-shape. They machined each branch at a different fluence in order to obtain different wettabilities (Figure 20) with the goal to control the fluid separation ratio in microfluidic devices. As can be seen in figure 21, the fluid front advances into the more hydrophilic branch quicker than into the other. Furthermore, the degree of separation increases if the difference in wettability between the two branches is increased. They also observed that the flow front was concave for hydrophilic channels and convex for hydrophobic channels. While their results indicate that surface hydrophilicity will lead to higher fluid velocities, this does not necessarily apply in the case of superhydrophobic materials that experience Cassie-Baxter state wetting.



Figure 21: Microfluidic junction with controlled separation ratio based on different wettabilities. Reproduced from [103].

As presented in section 2.3.2 and 2.4.1, raster scanning PTFE can lead to the formation of a superhydrophobic microstructure with excellent water repellency. In their study, Ahmmed et al. studied the drag reducing properties of such structures in microscale internal flow [110]. In Cassie-Baxter wetting, liquid sits on a composite surface composed of solid and trapped air pockets. In this case, during fluid flow over such a surface, the no slip boundary condition at the wall does not apply. There exists an effective slip velocity at the wall that causes drag reduction. This drag reduction is quantified by the slip length, which is the normal distance into the wall where the velocity would vanish based on the velocity profile. Ahmmed et al. measured slip lengths of 17 μm and 38 μm for water and a 30% solution of glycerol respectively when flowing over a lasermodified superhydrophobic PTFE structure in microscale internal flow. Thus, their results suggest that inducing superhydrophobicity in microchannels could lead to more efficient fluid transport due to drag reduction. However, PTFE is not suitable for lab-on-chip applications due to its opacity. Recently, Sarbada et al. have tested flow inside superhydrophobic PDMS microchannels [111]. They did not directly ablate the microchannel on the PDMS surface but rather machined a hierarchical superhydrophobic pattern onto a copper master which they then transferred to PDMS by hot embossing. The flowrate in the resulting microchannel (Figure 22) was measured to be

186% higher than for an untextured one thus confirming the drag reduction results of Ahmmed et al..



Figure 22: a) Photograph and b) scanning electron micrograph of a superhydrophobic PDMS microchannel. Reproduced from [111].

In conclusion, femtosecond laser micromachining is a promising tool for the fabrication of efficient microchannels for microfluidic lab-on-chip devices. Such devices typically contain micrometric photonic components for signal transport and sensing. Some of these can also be directly produced by femtosecond laser machining as discussed in the following section.

2.4.3 Optical applications

As described in section 2.2, femtosecond laser micromachining can effectively induce ablation in transparent materials through non-linear optical processes. Furthermore, modification is not limited to the surface of the material. Indeed, by focusing the incoming laser beam inside the bulk of a transparent material that does not absorb the incoming wavelength, femtosecond laser radiation can cause modification inside the bulk while leaving the surface intact. In some materials, irradiation below the ablation threshold can cause a localized increase in refractive index. If this change in optical properties is directionally induced inside the bulk of a transparent material, an optical waveguide can be fabricated. Zoubir et al. first attempted the fabrication of buried waveguides in PMMA [112]. Their experiments resulted in a tubular structure with an increased refractive index around its rim resulting in an annular waveguide. They attributed this shape to thermal expansion which densifies the material at the edge of the focal volume. Several later studies all reported the fabrication of PMMA waveguides with a circular transmission cross-

section where, as opposed to Zoubir et al.'s study, the irradiated material observes a positive refractive index change throughout the focal volume (Figure 23) [113-117]. However, Eaton et al. later compared PMMA waveguides to those in glass and found them to be inferior due to low refractive index changes, high damping losses, and temporal instabilities caused by the outward diffusion of photoinduced breakdown products [118]. Other structures that can be formed through laser-induced refractive index changes are diffraction gratings. Indeed, if the refractive index change is periodically induced within or on the surface of a material, volume or diffraction gratings can be respectively produced as successfully demonstrated by Wochnowski et al. on several polymers [119].



Figure 23: a) Top-view and b) cross-sectional transmission profile of buried waveguides in bulk PMMA. Reproduced from [117].

Other microphotonic components have also been inscribed on polymer surfaces by femtosecond laser machining such as binary Fresnel lenses. Binary Fresnel lenses are characterized by a large numerical aperture, short focal length, and high focusing efficiency (upper theoretical limit of 40%). Due to their simple geometry that consists of only two layers, they are much more compact than other lens types, thus making them ideal for implementation in micro-optical devices. While most research has been conducted on semi-conducting materials, Vazquez et al. successfully inscribed a binary Fresnel lens on PMMA by femtosecond laser ablation [120]. As can be seen in Figure 24, they produced a Fresnel lens with high feature spatial resolution. Furthermore, the authors optimized the operating parameters so as to obtain minimal roughness (50 nm) at the bottom of the ablated trenches to minimize losses in transparency. They also reported an optimized focusing efficiency of around 30% which is not far off from the theoretical upper limit. Figure 24c shows a photograph of white light being focused through the lens. As is typical for binary Fresnel lenses, different wavelengths are focused at different focal lengths which

is useful for optical signal filtration. Eaton et al. integrated the same design in a optofluidic chip and highlighted its use in fluorescence detection [118]. Guduru et al. later inscribed a similar design onto a one-dimensional photonic crystal but could only achieve an efficiency of 12.5% [121].



Figure 24: a) Top view, b) cross-sectional depth profile, and c) photograph (with wavelength separation of focused white light) of a 0.5 mm focal length binary Fresnel lens inscribed on PMMA. Reproduced from [120].

In addition to Fresnel lenses, convex microlens arrays have also been successfully produced by femtosecond laser machining. Meunier et al. were the first to achieve that by using a 76 MHz femtosecond laser [122, 123]. By focusing a beam with such a high repetition rate inside the bulk of PC, significant heat accumulation can occur which leads to vaporization and material expansion. By purposely inducing this heat accumulation right below the surface (50 µm), material expansion leads to surface swelling in the shape of a convex bump. And since the surface was not directly modified by the laser pulse, it retains the smoothness of the pristine material thus retaining its optical quality and forming a convex lens. Similar results were later obtained on PMMA by Shao et al. [124], Ou et al. [125], and Li et al. [126]. Laser-induced surface swelling could also be exploited for other purposes as highlighted by Joanni et al. [127]. In their study, surface swelling was directionally induced in the shape of lines on PMMA. The swollen ridges were then imprinted onto a PDMS surface so as to create microchannels similar to the ones described in section 2.4.2.

Finally, femtosecond laser micromachining polymers has also been gaining attention in the field of ophthalmology. After cataract surgery, an intraocular lens is typically inserted into the eye in order to restore vision. This lens is typically made out of a transparent flexible polymer such as PMMA. However, in some cases, diffractive aberrations and post-operation opacification of the lens can occur. The selective etching of small incisions into the lens can help mitigate these

complications. Furthermore, the inscription of a diffractive pattern into the center of the lens can increase the depth of focus and improve intermediate vision. Serafetinides et al. [128] and Roszkowska et al. [129] studied the micromachining of PMMA intraocular lenses. The latter state that the implementation of femtosecond laser technology in cataract surgery has helped reduce the use of surgical instruments inside the eye by 40%. Recently, Bille et al. have demonstrated that machining PMMA intraocular lenses in an aqueous environment can lead to a localized correction in refractive index [130]. This change is caused by the hydrolysis of ester bonds and could potentially be applied for the future optimization of intraocular lenses.

In summary, femtosecond laser-polymer interactions are governed by non-linear phenomena and changes in material optical properties. This has allowed the fabrication of novel photonic components in polymers such as waveguides and Fresnel lenses. The highly precise and non-intrusive nature of the machining process has also led to its implementation in the medical field. Other non-optical properties of laser-induced structures such as their high surface area and hierarchical roughness are also relevant in the biomedical field as will be discussed in the following section.

2.4.4 Biocompatibility enhancement

Polymers are widely used materials in the biomedical industry due to their flexibility. They are typically used in bone and dental implants, arterial grafts, and scaffolds for tissue engineering. However, they are typically biologically inert meaning that they offer little interaction with surrounding cells while used in vivo. This can inhibit the development of an extra-cellular matrix on their surface and thus inhibit cell attachment and growth. In some cases, this can lead to decreased mechanical stability, increased risk of infection, and revision surgery [131]. This can be remediated by modifying the surface properties such as topology, roughness, surface chemistry, and wettability [132]. An increased surface roughness generally enhances cell adhesion and affects gene expression but can also inhibit proliferation. On the other hand, surface hydrophilicity typically promotes cell adhesion but can either increase or decrease protein adsorption. Thus, surface optimization is heavily dependent on the targeted cell type [133]. Since femtosecond laser

micromachining can alter all of the abovementioned properties, several authors have investigated its effectiveness in enhancing cell attachment and growth on polymeric surfaces.

Most of the published literature focuses on the femtosecond laser texturing of biodegradable polymers such as PLA, and poly(caprolactone) (PCL). Their property is relevant for tissue engineering, where the scaffold needs to biodegrade over time in order to be gradually replaced by the growing tissue. Yeong et al. were the first to micromachine PLA with a femtosecond laser and study the resulting effect on surface-cell interactions [134]. In their study, trenches were machined into a PLA/PCL copolymer surface on which C2C12 myoblast cells were later grown. The cell culture showed strong adhesion on the textured surface, whereas it was detaching from a flat control surface. In addition, cells preferentially adhered on the machined trenches with little attachment on the non-textured space between them due the hierarchical roughness observed on the trench side walls. The cells also aligned themselves to be parallel to the machined trenches as opposed to the random orientation they adopted on the flat surface. Cell alignment is highly beneficial in cardiac tissue engineering as it allows the generation of effective vector contractile power. Li et al. machined a similar structure on the same polymer and obtained similar results with respect to preferential cell attachment and cell elongation [135]. The cells grown in their study were human mesenchymal stem cells. Interestingly, the stem cells grown on a textured surface had an altered gene expression with respect to the control group. Indeed, myogenic (muscle tissue) markers were up-regulated at the expense of osteogenic (bone tissue) and neurogenic (nervous tissue) markers. Thus, they experienced specific differentiation into a myogenic lineage. This was attributed to the cell elongation which increases the intracellular tension force and recruits a-smooth muscle actin to stress fibers. Cell preferential attachment, elongation, and differentiation were all observed to increase for smaller trench widths. Thus, optimizing the geometry of femtosecond laser-inscribed structures can help regulate stem cell gene expression on implants. Other studies with similar results with regard to cell attachment and elongation have been performed with breast cancer cells on PS and PLA [136], oral keratinocyte stem cells on a biodegradable polymer mix [137], U2OS cells on PC [138], and HL-1 cells on a conjugated polymer [139]. Similar microstructures have also been demonstrated to increase the adsorption of specific compounds found in extra-cellular matrices such as hyaluronic acid (Figure 25) [137], collagen, and laminin [140].



Figure 25: Attachment of fluorescent hyaluronic acid on a) flat control and b) fs laser micropatterned biodegradable polymer. Reproduced from [137].

Texturing has not been limited to planar substrates as some authors have studied the effect of femtosecond laser micromachining of porous electrospun PCL and PLA scaffolds that are typically used in tissue engineering [141]. Lee et al.'s study stands out as they actually tested their textured scaffolds in vivo by subcutaneously implanting them in rats [142]. Their results show that inscribing microhole arrays into the scaffold increased porosity, pore size, and provided an increased number of pathways between the different electrospun layer. After in vivo implementation, this led to increased macrophage and endothelial cell proliferation into the scaffold. Another in vivo study was performed by Guo et al. on poly(ether ether ketone) (PEEK) dental implants in rabbits [143]. Machining led to a large increase in surface area due to the formation of a hierarchical structure. This promoted osteogenesis when put in contact with bone in vivo and led to a larger adhesion strength when compared to the non-textured implant.

One thing to note is that not all laser machined polymer surfaces promote cell attachment. For example, the bioadheson of human cervical cancer cells on superhydrophobic surfaces created on PTFE (Figure 14) were tested by Liang et al. [3]. Their results have shown that, while cells could grow on the non-textured polymer, growth was impossible on the superhydrophobic structure due to the rejection of the cell culture medium by the air-trapping surface. This indicates that femtosecond laser-induced superhydrophobic polymer surfaces could have antibacterial properties which are relevant for the prevention of contamination in the food and medical industry or the prevention of biofouling in pipes.

In conclusion, femtosecond laser texturing of polymers can significantly affect the way cells interact with their surface. While several potential applications have been highlighted, the relationship between the machining process and observed results remain mostly empirical. Furthermore, with the exception of Liang et al's study [3], experiments have been limited to laser-inscribed geometries. If the dimensions of the porous laser-induced surface structures shown in Figures 14 and 15 are optimized on biocompatible polymers, this can lead to the single-step production of novel porous scaffolds on a wide variety of substrates. Thus, biocompatibility enhancement by femtosecond laser texturing of polymers is expected to be increasingly relevant as a field of research in the years to come.

2.5 Conclusions

In this chapter, a comprehensive review of femtosecond laser micromachining of polymer surfaces was presented. The intricacies of polymer-laser interactions have been highlighted including non-linear absorption, photochemical reactions, and incubation effects. The resulting microstructures including laser-inscribed and laser-induced structures have been highlighted. These novel topologies offer many interesting properties such as a hierarchical roughness and laser-induced porosity. An overview of the many applications where these properties can be exploited such as superhydrophobic materials, microfluidic devices, photonic components, and biomedical implants has also been given. Thus, we hope that this review will prove beneficial to the students and researchers in the field.

Chapter 3 Formation of porous networks on polymeric surfaces by femtosecond laser micromachining

3.1 Preface

Recently, our research group has reported the formation of a superhydrophobic porous structure on PTFE after femtosecond laser irradiation [3]. However, it is unknown if it is reproducible on other polymers. As a matter of fact, fs laser-induced structures on polymer surfaces have barely been investigated. Thus, in this chapter, six different polymers were machined at different conditions. As a consequence, the conditions and material-dependent parameters that favor the formation of fs laser-induced structures were identified. These results were used as a basis for a later study were the properties of these structures were characterized. This chapter is a reproduction of a proceedings article published as part of the SPIE LASE conference held in San Francisco in January 2017. The supplementary data for this study can be found in Appendix A. It contains the lacunarity curves, modified depth measurements, and line width measurements that are not shown in this chapter. The complete citation of the published proceedings article is:

Y. Assaf, A.-M. Kietzig, Formation of porous networks on polymeric surfaces by femtosecond laser micromachining, SPIE LASE, SPIE, 2017, p. 11.

Formation of porous networks on polymeric surfaces by femtosecond laser micromachining

Youssef Assaf, Anne-Marie Kietzig

Abstract

In this study, porous network structures were successfully created on various polymer surfaces by femtosecond laser micromachining. Six different polymers (poly(tetrafluoroethylene) (PTFE), poly(methyl methacrylate) (PMMA), high density poly(ethylene) (HDPE), poly(lactic acid) (PLA), poly(carbonate) (PC), and poly(ethylene terephthalate) (PET)) were machined at different fluences and pulse numbers, and the resulting structures were identified and compared by lacunarity analysis. At low fluence and pulse numbers, porous networks were confirmed to form on all materials except PLA. Furthermore, all networks except for PMMA were shown to bundle up at high fluence and pulse numbers. In the case of PC, a complete breakdown of the structure at such conditions was observed. Operation slightly above threshold fluence and at low pulse numbers is therefore recommended for porous network formation. Finally, the thickness over which these structures formed was measured and compared to two intrinsic material dependent parameters: the single pulse threshold fluence and the incubation coefficient. Results indicate that a lower threshold fluence at operating conditions favors material removal over structure formation and is hence detrimental to porous network formation. Favorable machining conditions and material-dependent parameters for the formation of porous networks on polymer surfaces have thus been identified.

3.2 Introduction

Polymers have been extensively used as biomaterials due to their desirable bulk properties such as elasticity and degradability [144]. However, applications that require enhanced cell attachment and growth such as stents [11] and grafts [12] are heavily dependent on surface properties. High porosity, enhanced surface area, and multi-scale roughness are desirable for such applications, and significant effort has been made in order to impart those properties to polymeric surfaces [145]. Lithography, which is the current industry standard for polymer surface patterning and modification, only partially achieves that goal. While it successfully enhances surface area, achieving hierarchical roughness requires a multi-step process involving iterative layer-by-layer coating and exposure that does not typically induce porosity [146].

With the emergence of femtosecond (fs) technology, laser micromachining is now able to introduce dual scale roughness (both micro- and nano-) on target surfaces [2]. Furthermore, it is a single-step, non-contact method that delivers energy in pulses of such small duration that heat-induced damage to the material is minimized [1].

Ultrashort laser-polymer interaction is still under investigation as many photochemical [60] and non-linear optical processes [57] are involved. As a result, most of the current literature concerning fs polymer machining focuses on hole or line ablation in the aim of studying local polymer interaction with a select number of laser pulses as opposed to machining over a large area. However, laser-induced porosity on polymer surfaces has been observed on the bottom or side walls of inscribed craters and lines in the past. For example, fibre-like structure formation on the side walls of PTFE ablation craters has been reported in several studies [147-149]. In addition, several publications have reported the appearance of micro-pores on PMMA [13, 14, 16] and PC [15] after fs laser hole and line ablation.

This aspect of polymer laser ablation has been mostly reported as an unsuspected side effect of machining and it is unclear how it would affect surface topology when machining over an area. Baset et. al's (2013) recent study of PMMA ablation is one of the few publications focusing on fs laser induced porosity on polymer surfaces [16]. Their results have shown that the porous area fraction is dependent on pulse energy as well as number of pulses for hole ablation and scanning speed for line ablation. This type of porosity could therefore be controllable by adjusting machining parameters. Recently, Liang et al. (2014) successfully produced a novel porous network

structure on PTFE by fs laser micromachining over a large area [3]. Their machining technique led to the formation of a fibrillary network that gets increasingly entangled as a function of fluence. However, very little is known about the formation mechanisms or even the properties of such structures. In addition, no information about the depth over which these structures form is given. Furthermore, it has not yet been established if this type of network can be reproduced on other polymers which might be more suitable for in-vivo use than PTFE.

In summary, fs laser induced micro-porosity has been observed on several polymers. In the case of PTFE, it leads to the formation of a porous network structure when homogeneously machining the surface over an area. This study aims at studying fs laser area machining of a variety of polymers in order to identify which machining conditions and material-dependent parameters are favorable for the formation of porous networks.

3.3 Materials and methods

3.3.1 Materials:

The following six polymers were studied: poly(tetrafluoroethylene) (PTFE), poly(methyl methacrylate) (PMMA), high density poly(ethylene) (HDPE), poly(lactic acid) (PLA), poly(carbonate) (PC), and poly(ethylene terephthalate) (PET). For each material, 3 by 3 mm square samples were cut out from a commercially available sheet (McMaster-Carr). The samples were 1.5 mm thick with the exception of PLA (0.9 mm) and PTFE (3 mm).

3.3.2 Laser micromachining:

The samples were micromachined using an amplified Ti:sapphire solid-state laser (Coherent Libra) which emits a horizontally polarized Gaussian beam of 800 nm wavelength, 4 W output power, and in pulses of 85 fs duration. It was operated at a repetition rate of 1 kHz. The beam power is controlled through a variable attenuator which consists of a half-wave plate and a polarizing beam splitter. The beam is then focused using a 100 mm plano-convex lens down to a theoretical $1/e^2$ spot size of 44 µm onto a motorized 3D translational stage (Newport Corporation) which is subjected to the stationary laser beam. The stage's movement and velocity were digitally controlled via the GOL3D software (GBC&S) along with a mechanical shutter (Uniblitz) in order to create different machining patterns. Lines were machined by moving the stage in the horizontal

direction while patches were created by vertically overlapping lines in a raster scan pattern. The samples' surfaces were placed at the focal plane of the lens. Immediately after machining, all samples were placed in a sonication ethanol bath for five minutes to remove any loose machining debris.

3.3.3 Machining parameters:

Two types of machining experiments were performed. Line scans for the determination of material dependent parameters and raster scans for microstructure identification. The pulse peak fluence F_0 and pulse-per-spot number *PPS* were used as variable parameters. The latter was calculated as follows:

$$PPS = \left(\frac{\omega_0 f_p}{v}\right) \left(\frac{1}{1 - \Phi}\right). \tag{20}$$

Where ω_0 represents the theoretical beam diameter, f_p the laser's repetition rate, v the scanning velocity and Φ the vertical overlap between two raster scanned lines (equal to zero for a line scan).

For each polymer, 40 lines were machined at the conditions corresponding to all the possible combinations of F_0 and *PPS* presented in Table 2. In addition, 30 patches were machined on each of the six polymers corresponding to a combination of 10 F_0 values (same as Table 2) and 3 *PPS* values (listed in Table 3). All of these conditions were confirmed to result in a homogeneous fluence profile according to the accumulated fluence profile (AFP) model following a procedure outlined in Ahmmed et al.'s (2015) recent work [150].

Table 2: Line ablation machining parameters	Table 2:	Line	ablation	machining	parameters
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 Power (mW)	Corresponding F ₀ (J/cm ²)	v (mm/s)	Corresponding PPS
1.5	0.2	0.22	200
4.4	0.6	2.2	20
9.9	1.3	4.4	10
17	2.2	33	1 ^a
25	3.3		
34	4.5		
44	5.8		
54	7.2		
65	8.5		
76	10		

a- This velocity actually corresponds to a *PPS* number of 1.3 and was the highest velocity achievable with our setup. However, this condition was considered equal to a *PPS* of 1 since all of the presented results were measured at the center of an ablated hole which is unaffected by the pulse overlap at the hole's edges.

Table 3: PPS parameters for patch ablation.

v (mm/s)	Φ	PPS
4	0.95	220
8	0.95	110
16	0.95	55

3.3.4 Topography imaging, measurements, and analysis:

Line width was measured by 3D confocal microscopy (Olympus LEXT OLS4000). The surface topography was imaged via scanning electron microscopy (SEM) (FEI Inspect F50). This required coating the samples with a 10 nm thick layer of gold by low-vacuum sputtering in order

to avoid surface charging. SEM micrographs were quantitatively analyzed by using the Fraclac plugin for the ImageJ image analysis software [151].

3.3.5 Microstructure thickness determination:

The micromachined square patches of interest were cut in half perpendicularly to scanning direction with a diamond saw blade. The resulting cross-section was polished with 1200 grit silicon carbide sandpaper. The depth of removed material and the microstructure thickness was then determined by imaging with an environmental scanning electron microscope (FEI Quanta 450).



Figure 26: Microstructure thickness determination.

As seen in Figure 26, two thicknesses were measured: l_{ab} which represents the thickness of the layer of ablated material, and l_{ms} which represents the thickness of the microstructure itself. Their sum l_{tot} represents the total depth of affected material.

3.3.6 Lacunarity analysis:

Microstructure identification and comparison is usually qualitative and involves a visual assessment of SEM micrographs. In this study, the presented microstructures are quantitatively compared by lacunarity measurements on their SEM images. Lacunarity is typically calculated by the sliding-box counting algorithm [152], in which a box of dimension r^*r slides across a binary image. The number of foreground pixels in that box is measured at each position along the image and a distribution is generated. The lacunarity λ_{lac} of the image can then be calculated from this distribution:

$$\lambda_{lac}(r) = \left(\frac{s_k(r)}{\bar{k}(r)}\right)^2 + 1.$$
(21)

where s_k and \overline{k} represent the standard deviation and mean of the foreground pixel distribution at a given box size r. A higher lacunarity value means an image is spatially coarse or clumped while a lower value corresponds to a fine texture. From equation 21, it is evident that λ_{lac} is highly dependent on the box size r. Therefore, when comparing two SEM images, looking at lacunarity values at a single r does not necessarily reflect the overall texture. One way to generate a single lacunarity parameter is to calculate the area under the $\ln(\lambda_{lac})$ vs. $\ln(r)$ curve [153]:

$$\Theta = \int_0^{\ln M} \ln(\lambda_{lac}) \, \mathrm{dln}(r). \tag{22}$$

where *M* corresponds to the smaller dimension of the image being analyzed and θ is termed as the spatial heterogeneity index. Recent publications have shown that θ allows for the objective characterization and comparison of hierarchical surface topographies [154, 155]. This approach was therefore used in this study.

SEM micrographs at 10,000x magnification were taken for every machined patch before being converted into binary images for lacunarity analysis. The conversion was performed by first equalizing the images' histograms and then applying a threshold of 0.5 to ensure the same amount of foreground and background pixels. This method is evidently dependent on the focus and contrast of the images in question so substantial effort was made in order to minimize these effects by collecting micrographs of similar quality. After the conversion was made, the $\lambda_{lac}(r)$ function and the associated Θ were calculated for every image.

3.4 Results and discussion

At low fluence (F_0 =1.3 J/cm²), all of the materials except PLA form a porous network structure (Figure 27). In contrast, machining only seems to impart a randomly distributed roughness on PLA which does not noticeably change with fluence. For the rest of the materials, a large divergence in behaviors can be observed at high fluence (F_0 =10 J/cm²). PMMA seems to be the least affected by increasing fluence since the microstructure remains almost identical. HDPE, PTFE, and PET exhibit an increasingly larger degree of bundling of the network structure which leads to an apparent loss in porosity. PC does show some degree of bundling at intermediate fluences but quickly observes a complete breakdown of the network which transitions into a blocky structure. All of these trends were numerically validated through lacunarity analysis. Figure 28
illustrates the evolution of the lacunarity function exemplarily for PET as a function of fluence at a *PPS* number of 55.



Figure 27: Microstructure topologies at PPS=55.



Figure 28: Lacunarity curves at different fluences for PET at PPS=55.

The plot clearly displays an increase in spatial heterogeneity for PET as a function of fluence. Indeed, the spatial heterogeneity index steadily increases from Θ =1.3 at F_0 =1.3 J/cm² to Θ =1.54 at F_0 =10 J/cm². This corresponds to a texture that is becoming increasingly coarse or clumped which actually confirms our observation of the structure bundling up.

Intra-material comparisons can be easily made since it is straightforward to obtain images that have similar contrast and brightness within the same material. However, inter-material comparisons are less effective. Even if similar focus and contrast can be achieved, the information depth of the pixels will be different due to the properties of the polymers, their interaction with the SEM beam, and the different topologies studied. Therefore, even if some microstructures exhibit similar trends with respect to fluence across materials, their spatial heterogeneity indices will not be comparable. For this reason, for every material, all of the indices were normalized with respect to the index corresponding to the lowest fluence where ablation occurred (F_0 =1.3 J/cm² for all polymers). The evolution of the normalized index $||\theta||$ as a function of fluence can therefore be compared for all materials while eliminating the effects mentioned above (Figure 29a).



Figure 29: a) Normalized spatial heterogeneity index as a function of fluence at PPS=55. b) Normalized spatial heterogeneity index as a function of PPS at $F_0=3.3$ J/cm². The dashed lines only serve as visual guidelines.

This approach confirms our previous qualitative assessment of the microstructure. The bundling of the structure with fluence for HDPE, PTFE, and PET is translated into a steady increase in the heterogeneity index. Furthermore, the plot also demonstrates that the degree of bundling is higher for PET than for PTFE which in turn is higher than that of HDPE. PC follows a similar trend up to F_0 =5.8 J/cm². At higher fluences, the transition into the blocky structure translates into a very sharp decrease in Θ . Finally, the stability of the microstructure with respect to fluence for PLA and PMMA is also confirmed as the normalized indices for these two materials hover between the values of 1 and 0.95 (albeit with a slightly decreasing trend). The agreement between our assessment of the SEM images and the quantitative data lead us to conclude that lacunarity analysis is a tool that can objectively characterize and compare fs laser induced microstructures on polymeric surfaces.

All of the results presented so far have been for a fixed *PPS* number of 55. The reason for that is that the effect of *PPS* on microstructure was observed to be extremely similar to the effect of fluence. Figure 29b shows the evolution of lacunarity data with increasing *PPS* numbers for F_0 =3.3 J/cm². For this plot, the indices were normalized by the value at *PPS*=55 for each material. By comparison with figure 29a, it is evident that pulse number has the same qualitative effect on microstructure as fluence.

In conclusion, this parametric study shows that, with the exception of PMMA, operation at high fluence and pulse numbers is detrimental to porous network formation as it leads to bundling and increased structure coarseness or even complete structure breakdown in the case of PC.

Therefore, operation slightly above a polymer's threshold fluence is recommended when aiming to avoid the abovementioned phenomena. PMMA's singular behavior indicates that one of its intrinsic material properties renders it resistant to structure bundling at high fluence. Its outstanding resistance to photo-oxidation [156] might indicate that porous network breakdown is related to photo-reactive processes.

After the identification of the different topologies, the depth over which the microstructures have formed was measured according to the procedure described in section 3.3.5. Figure 30 displays the results for PC at *PPS*=55.



Figure 30: Modified depth as a function of fluence for PC patches at PPS=55. The error bars represent the standard deviation of three measurements.

As can be seen, both the thickness of the microstructure l_{ms} and the ablated thickness l_{ab} linearly increase as a function of $\ln(F_0)$. For all materials, l_{ms} values ranged between 3 and 50 µm within the range of our experiments. Furthermore, microstructure formation seems to occur over a length comparable to material ablation for all conditions as l_{ms} and l_{ab} are almost equal and correspond to approximately half of l_{tot} . In other words, the average ratio of l_{ab} over l_{tot} shows whether material removal or microstructure formation is the dominant mechanism for each material. As can be seen in Table 4, HDPE, PMMA, and PTFE displayed a similar behavior to PC with their $\overline{l_{ab}/l_{tot}}$ ratio being close to 0.5. The only materials where one of the mechanisms was dominant over the other were PLA and PET. For these two polymers, material is removed over a

thickness that is significantly larger than the thickness of the microstructure formed. This discrepancy across materials can be explained by their threshold fluence at operating conditions (F_{th} at PPS=55) which is also found in Table 4.

Material	$\overline{l_{ab}/l_{tot}}$	$F_{th}(1) (\mathrm{J/cm}^2)$	ξ	F_{th} (55) (J/cm ²)
	0 (2	1.24	0.(2	0.28
PET	0.62	2.15	0.62	0.28
РС	0.53	1.83	0.73	0.60
HDPE	0.51	1.25	0.85	0.67
РММА	0.49	2.50	0.74	0.89
PTFE	0.47	2.11	0.82	1.01

Table 4: Ablation Parameters and extent of material removal.



Figure 31: Line width results for PLA. The error bars represent the standard deviation of three measurements. The dashed lines represent the best fit of equation 23.

The threshold fluence F_{th} at each *PPS* was determined by fitting line width data (*D*) to Liu et al.'s model [73]:

$$D^2 = \frac{1}{2} \omega_0^2 \ln\left(\frac{F_0}{F_{th}(PPS)}\right). \tag{23}$$

The incubation model first introduced by Jee et al. [52] then allowed us to determine the single pulse $F_{th}(1)$ value as well as the incubation coefficient ξ (Table 4):

$$F_{th}(PPS) = F_{th}(1)PPS^{\zeta-1}.$$
(24)

Figure 31 presents the results for PLA. The threshold fluence at 55 *PPS*, which corresponds to the actual machining conditions for area modification, was then calculated using equation 24 (Table 4). By comparing this parameter to the average ratio of l_{ab} over l_{tot} , we can clearly see that the extent of material removal is correlated to the threshold fluence at operating conditions. Indeed, materials with a high single pulse threshold fluence such as PMMA, a high incubation coefficient such as HDPE, or a combination of both such as PTFE have a higher threshold fluence at 55 *PPS* and are therefore less susceptible to material removal. On the other hand, PLA and PET both displayed an extremely low incubation coefficient which led to a very low threshold fluence at 55 *PPS*. In the specific case of PLA, the resulting threshold fluence is significantly lower than for all other polymers. As a result, even when operating at low fluence, almost all of the incoming energy can be converted into material ablation. This explains why no significant structure formation was observed on PLA using our machining technique. And since homogeneous area machining typically requires operation at high overlap and therefore high *PPS*, having a low incubation coefficient is detrimental to porous network formation since it will lead to a lower threshold fluence at operating conditions and limited structure formation.

3.5 Conclusion

The microstructures formed on six different polymers after femtosecond laser area machining were studied. Patches were machined on all polymers at several fluence and pulse number conditions. Lacunarity analysis identified several behaviors. Porous network structures were confirmed to form at low fluence on all polymers except PLA. PET, PTFE, and HDPE observed a bundling up of their structure with fluence. PC observed the same type of behavior in addition to the formation of a cracked structure at high fluence. PLA exhibited no microstructure formation. The evolution of microstructure as a function of pulse number followed the same trends. Operation at low pulse numbers and slightly above the threshold fluence is therefore recommended for porous network formation. The evolution of microstructure depth with respect to fluence

showed that its extent is dependent on the material's threshold fluence at operating conditions. The latter was calculated by gathering the single pulse threshold fluence and incubation coefficients for all materials through line ablation experiments. As observed for materials with low incubation coefficient such as PLA and PET, a low threshold fluence can lead to increased material removal which can inhibit microstructure formation.

This study confirmed the possibility of porous network formation on several polymers at different machining conditions. Furthermore, several guidelines with regards to their design were given which significantly contributes to future optimization studies.

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Chapter 4 Optical and Chemical Effects Governing Femtosecond Laser-Induced Structure Formation on Polymer Surfaces

4.1 Preface

Our previous study confirmed that femtosecond laser-induced porous structures can form on a wide variety of polymers. However, their formation mechanism is not well understood. Due to the many photochemical and non-linear optical processes involved, their optical and chemical properties are expected to be different from those of the base material. This is why, in this study, a detailed optical and chemical characterization of the fs laser induced structures that form at two different wavelengths was performed. This allowed the identification of the optical and chemical phenomena that govern fs laser-induced microstructure formation on polymers. This chapter is a reproduction of an article published in the journal Materials Today Communications. The supplementary data for this study can be found in Appendix B. It contains the transmittance spectra and depth measurements not shown in this chapter. The complete citation of the published article is:

Y. Assaf, A.-M. Kietzig, Optical and chemical effects governing femtosecond laser-induced structure formation on polymer surfaces, Materials Today Communications 14 (2018) 169-179.

Optical and Chemical Effects Governing Femtosecond Laser-Induced Structure Formation on Polymer Surfaces

Youssef Assaf, Anne-Marie Kietzig

Abstract

With the emergence of femtosecond technology, laser machining has recently led to the creation of novel porous structures on polymers. However, the mechanism behind their formation is yet to be understood. In this study, the dependence of femtosecond laser-induced surface structure on processing parameters is established at two distinct wavelengths (800 nm and 275 nm) for six different polymer films: LDPE, PC, PET, PLA, PMMA, and PTFE. All of the observed structures are then optically and chemically characterized as a first step towards elucidating their formation mechanism. The threshold fluence at operating conditions was determined to be the main parameter affecting porosity formation during machining. Furthermore, for transparent films, a transition from multiphoton to linear absorption is observed to occur at 800 nm but not at 275 nm. This shift in optical properties was determined to be a major contributor to incubation effects. These observations are also in agreement with UV-VIS analysis as measurements show that polymers with a cut-off wavelength lower than that of the laser beam undergo a shift in absorption behavior. Finally, some polymers experience a continuous darkening of their surface with increasing fluence due to an increasing degree of photo-oxidation.

4.2 Introduction

Laser micromachining is a single-step, contactless method to alter the structure and properties of a material's surface [1]. With the emergence of femtosecond (fs) laser technology, this technique now allows the impartation of hierarchical roughness to target surfaces down to the nano-scale [2]. This sets it apart from other surface texturing techniques like etching and lithography since any micro-scale pattern that is inscribed into the surface through material ablation will further exhibit nanometric features without the need for an additional processing step [146]. In addition to such laser-inscribed structures, subjecting a surface to femtosecond laser radiation can lead to self-assembled structures with dimensions smaller than the focal spot size [88]. Such laser-induced microstructures have been extensively studied on metals due to their unique topography. For example, laser-induced periodic surface structures (or LIPSS) and hierarchical topologies can be used for the generation of structural color [157] or superhydrophobic surfaces [158-160] respectively. Thus, through the creation of unique laser-induced structures, fs laser micromachining now allows the development of engineered metal surfaces with completely novel properties. In contrast, very few studies describe the production of laser-induced surface structures on polymers. Some notable examples include Baudach et al.'s (2000) observation of bubble formation on PC and PMMA after machining [15] and Yada et al.'s (2015) study of LIPSS formation on PLA [9]. The aim of this study is therefore to characterize the different laser-induced microstructures that appear on polymer surfaces under different machining conditions as a first step towards elucidating their formation mechanism. The polymers chosen for this study were films of: low density poly(ethylene) (LDPE), poly(lactic acid) (PLA), poly(carbonate) (PC), (PET), poly(ethylene terephthalate) poly(methyl methacrylate) (PMMA), and poly(tetrafluoroethylene) (PTFE). In addition to their wide commercial availability, they contain a variety of chemical functional groups that will allow a better identification of the effect of chemical composition on machining results. Finally, their respective optical properties are varied enough so that the effect of the latter on machining results can be determined.

The most commonly reported laser-induced structures on polymers are LIPSS whose orientation is dependent on the incoming light polarization [53, 91]. Another feature of interest is laser-induced porosity, which has been observed to appear on PMMA [16, 70] and PC [70]. This

phenomenon was first described by Baudach et al. (2000) and was attributed to bubble formation during melt re-solidification. The aforementioned studies were mostly interested in fundamental laser-polymer interaction and therefore only described local structure formation on the bottom or side-walls of ablated craters as opposed to texturing an area larger than the focal spot size. Recently, Liang et al. (2014) have demonstrated that homogeneously texturing poly(tetrafluoroethylene) (PTFE) leads to the formation of an air-trapping porous structure that is effectively superhydrophobic [3]. Since then, our recent work has shown that similar structures can form on a wide variety of polymers [94]. Such structures, that are both porous and exhibit a dual-scale roughness, are prime candidates for applications where a large surface area is required; especially in the biomedical field where these properties can enhance cell adhesion and growth on scaffolds and grafts. Indeed Martinez et al. (2011) reviewed how enhancing surface roughness can lead to the increased endothelialization of stents [11]. Furthermore, in their review, Rashid et al. (2004) state that microporosity in synthetic grafts can help increase healing and angiogenesis [12]. However, the properties of such high surface area structures as well as their formation mechanism is still unknown. Due to the complex nature of laser-polymer interactions, these novel structures are expected to have properties that are significantly different from the base material because of the defects generated during laser irradiation. These defects might have a physical origin due to a local increase in absorption [57] or a chemical origin due to preferential bond breaking [10]. Literature suggests that such phenomena might also be highly dependent on wavelength [8] or photochemical reactions that occur during machining [42, 43, 45]. The sum of these processes makes polymers very sensitive to pulse number. This dependence is generally termed as incubation effects and was first observed to occur for a polymer in Baudach et al'.s study (1999) of poly(imide) ablation [87]. In summary, optical and chemical properties are essential parameters that not only dictate polymer machining behavior, but also change during the process. Tracking the evolution of these properties as a function of machining conditions will therefore offer substantial insight into the mechanisms at play. Such a comprehensive optical and chemical characterization of fs laser-induced structures on a variety of polymers will therefore give significant insight into their formation mechanisms. This improved understanding of the process will later allow the optimization of machining conditions in order to obtain structures with specific physico-chemical properties.

Our study therefore focuses on machining various polymers at two different wavelengths: λ =275 nm and λ =800 nm. These values were chosen because most of the studied polymers have their cut-off wavelength located in between these two values thus allowing us to determine the effect of band gap value on machining. The resulting structures were characterized by measuring their transmittance, reflectivity, chemical composition, and bonding structure. The threshold fluence and incubation coefficient of all materials were also measured at both wavelengths in order to observe if they are correlated to any of the aforementioned properties. All of the abovementioned measurements were then related to absorption mechanisms and photochemical pathways in order to determine the processes governing the formation of fs laser-induced structures on polymer surfaces.

4.3 Materials and methods

4.3.1 Materials:

For each polymer, 3x10 cm samples were cut from films with different thicknesses: $50 \mu m$ for PMMA (Evonik Industries) and LDPE (3Spack laboratory), 75 μm for PLA (BI-AX International Inc.), and 100 μm for the rest (McMaster-Carr).

4.3.2 Laser micromachining:

Samples were machined using a Ti:Sapphire laser (Coherent Libra) delivering a Gaussian beam at a wavelength of 800 nm and in pulses of duration τ =85 fs at a repetition f_p of 1 kHz (Table 5). For operation at 800 nm, the beam power was attenuated down to the desired operating power *P* through a digitally controlled half-wave plate and a polarizing beam splitter. The beam was then focused through a 100 mm lens down to a 44 µm spot size ω_0 onto the sample whose surface lied at the focal plane. The value of ω_0 was obtained by machining lines and fitting their measured widths to Liu et al.'s (1982) model [73]. The sample was placed on a digitally controlled stage (Newport corporation), whose trajectory and velocity v were controlled through the GOL3D software (GBC&S). For operation at 275 nm, the beam was passed through an optical parametric amplifier (Coherent Opera Solo) where the desired wavelength was produced. Similarly, the beam was attenuated through a variable neutral density filter (Newport corporation) before being focused through a 175 mm lens down to a 35 µm spot size. For this beam path, the sample was also machined at focus and positioned on another motorized stage (Zaber Technologies Inc.). For single pulse ablation, the beam was further passed through a selective beam chopper that effectively reduced the beam repetition rate down to 25 Hz. Finally, all samples were subjected to a five minute ethanol sonication bath immediately after machining in order to get rid of any loose machining debris.

Table 5: Laser characteristics.

Gain medium	Profile	λ (nm)	τ (fs)	f_p (kHz)	ω₀ (μm) for λ=800 nm	ω₀ (μm) for λ=275 nm
Ti:sapphire	Gaussian	800/275	85	1	44	35

Laser-induced structures were created by raster scanning the sample at different single pulse peak fluences F_0 (equation 25) and at a pulses-per-spot number *PPS* of 55 (equation 26) over a square area with dimensions 14x14 mm. The spatial overlap Φ between two consecutive lines in the raster scan was kept fixed at 0.95 in order to ensure a homogeneous structure.

$$F_0 = \frac{8P}{\pi \omega_0^2 f_p} \tag{25}$$

$$PPS = \frac{\omega_0 f_p}{\nu(1-\phi)} \tag{26}$$

As previously mentioned, due to incubation effects, the threshold fluence F_{th} is a function of *PPS*. The magnitude of this dependence is dictated by the material-specific parameter ξ , which is termed as the incubation coefficient. The single pulse threshold fluence $F_{th}(1)$ and ξ were obtained for each material by machining lines at different F_0 (equation 25) and *PPS* (equation 26 with Φ set to 0). At each *PPS*, the logarithmic dependence of the depth-per-pulse *d* on F_0 was then fit to equation 27 in order to obtain F_{th} and the effective absorption coefficient α_{eff} of the material.

$$d = \frac{1}{\alpha_{eff}} \ln(\frac{F_0}{F_{th}}) \tag{27}$$

 $F_{th}(1)$ and ξ are finally calculated by fitting the dependence of F_{th} on *PPS* according to the incubation model developed by Jee et al. (1988) (equation 28) [52].

$$F_{th}(PPS) = F_{th}(1)PPS^{\xi-1}$$
(28)

4.3.3 Topographical characterization:

Structures were imaged by scanning electron microscopy (SEM) (FEI Inspect F50) by sputter coating the samples with a 10 nm layer of gold in order to avoid surface charging. For the threshold determination experiments, ablation depths were measured by 3D confocal microscopy (Olympus LEXT OLS4000).

4.3.4 Optical characterization:

Optical characterization of the various films was performed with ultraviolet-visible spectrophotometry (UV-VIS) in transmittance mode (Thermoscientific Evolution 300). The instrument was fitted with an absorbent screen containing a circular aperture (3 mm diameter) to ensure that the incoming light is only passing through the machined area of interest. The 100% transmittance baseline was measured in air with the aperture installed. Reflectance measurements were performed with an integrating sphere accessory (Cary 100) internally coated with barium sulfate paint and using Spectralon® standard disks (Labsphere) for the 100% reflectivity baseline. An integration time of 15 seconds was used for each measurement in order to minimize the effect of noise.

4.3.5 Chemical characterization:

Chemical characterization of the various films was performed by X-ray photoelectron spectroscopy (XPS) (Thermoscientific K-alpha). Measurements were taken using a 400 µm spot size with an Argon ion flood gun turned on in order to compensate for surface charging. Two types of scans were performed for each sample. A survey scan (200 eV pass energy, 3 scans, 10 ms dwell time) in order to determine composition and high resolution scans (50 eV pass energy, 10 scans, 50 ms dwell time) for the 1s sublevel of Carbon, Oxygen, and Fluorine (PTFE only) in order to determine bonding structure. Peak allocation for the base materials was based on Beamson and Briggs' database [161]. Therefore, the same background subtraction method (linear) and peak fitting function (Gaussian-Lorentzian sum) were used. All samples were stored in a vacuum oven set at 30°C prior to analysis to ensure their dryness.

4.4 Results and discussion

4.4.1 Initial observations:

Figure 32 illustrates the different laser-induced structures obtained at 800 nm as well as the color change associated with their appearance. For all materials, no ablation was observed below $F_0=1.3 \text{ J/cm}^2$. Above that fluence, a porous structure appears on all polymers which makes them lose their transparency and gives them a light color ranging from white (PTFE, PLA) to light brown (PC). For PC and PET, the structure seems to form nanoparticle clusters at higher fluences and, in the case of PC, eventually leads to a loss in porosity. LDPE structure seems to be affected as well since the structure bundles up as fluence increases. Looking at the sample colors, we can see that all three of these polymers undergo a progressive darkening of their surface, with PC eventually becoming black. Furthermore, these three polymers are the only ones who experience a darkening before the ablation threshold is reached. Indeed, at $F_0=0.6 \text{ J/cm}^2$, a darkening is observed even though no structure has appeared yet. Finally, PLA, PMMA, and PTFE had both their color and structure unaffected by increasing fluence.



Figure 32: SEMs of laser induced microstructures at different fluences for a wavelength of 800 nm. All scale bars represent 4 μ m. Inset is a 3x3 mm photograph of the sample placed on white paper on which letters were printed to highlight the change in transparency.



Figure 33: SEMs of laser induced microstructures at different fluences for a wavelength of 275 nm. All scale bars represent 4 μ m. Inset is a 3x3 mm photograph of the sample placed on white paper on which letters were printed to highlight the change in transparency.

As illustrated in Figure 33, machining at a wavelength of 275 nm resulted in significantly different microstructures. First of all, for all polymers, structures appeared at a lower fluence than at 800 nm indicating a decrease in threshold fluence. PTFE is the only material that exhibited a similar porous microstructure and color at both wavelengths. While a porous structure still formed for LDPE, new circular features appeared during UV ablation. As seen on the SEMs, starting at F_0 =4.5 J/cm², certain regions of the surface underwent increased ablation with circular craters of around 4 µm starting to appear in between the typical porous structure. For the rest of the materials, the surface exhibits significant melt with limited porosity. Some nanoparticle cluster formation is observed on PC while the structures on PET looks like melt bumps that transition into grooves at higher fluence. The limited microstructure formation is also reflected in the color of the samples as they retain their transparency to different degrees indicating that only a shallow melt layer remained after ablation. Overall, visual inspection of the samples indicated that a significant change in optical properties was occurring during machining. So, as a first step, UV-VIS spectrometry was performed on all samples in order to track the evolution of those properties as a function of machining parameters.

4.4.2 Optical characterization:

For all materials, a very large decrease in transmittance was observed when the ablation threshold was reached. Figure 34 exemplarily presents the resulting spectra for PC.



Figure 34: Evolution of the transmittance spectrum of PC as a function of fluence.

The transmittance spectrum for non-machined PC is typical of a dielectric material. The material is fully absorbent below its cut-off wavelength λ_c =281 nm while it transmits almost all of the incoming light above that value. The optical bandgap energy of the material therefore corresponds to the energy of a photon having a wavelength of λ_c . The number of photons that need to be absorbed simultaneously in order to overcome that bandgap at any given wavelength λ is therefore equal to the rounded-up ratio of λ and λ_c . This value is thus equivalent to the order of the dominating multiphoton absorption process *m*. In the case of PC, for a wavelength λ =800 nm, this corresponds to *m*=3 and a 3-photon absorption process. However, Figure 34 clearly indicates a shift in absorption behavior with increasing machining fluence. Indeed, the original step-like spectrum gradually shifts until almost reaching a completely flat line at F_0 =5.8 J/cm². The latter is typical of absorbing materials. This is clear indication that the optical properties of the formed microstructure are very different from those of the original material.

Figure 35 summarizes both the transmittance and the reflectance data at λ =800 nm and λ =275 nm for the polymers machined at the respective wavelengths. At λ =800 nm, for all materials, a significant increase in reflectance is observed when the threshold for ablation is reached (F_0 =1.3 J/cm²). As can be seen in Figure 32, this corresponds to the appearance of the porous structure. Its roughness is therefore enhancing the scattering and diffuse reflection of all incoming visible

wavelengths giving most of the films a white appearance. At the same time, an even larger decrease in transmittance is observed. This confirms the fact that the laser-induced structures, unlike the transparent original materials, are actually absorbent with respect to the machining wavelength. While these observations apply to all polymers, two main groups can be distinguished. For PLA, PMMA, and PTFE, the optical properties do not seem to be affected by increasing fluence beyond the ablation threshold as their reflectance and transmittance remain somewhat constant. On the other hand, for LDPE, PET, and PC, reflectance and transmittance are continuously decreasing with fluence. This indicates that, not only are the laser-induced structures more absorbent that the original material, they are also becoming more and more absorbent as fluence increases. Furthermore, unlike the previous three polymers, these materials also experience a significant drop in transmittance before the ablation threshold is reached ($F_0=0.6 \text{ J/cm}^2$). This phenomenon can be observed in Figure 32, where the films exhibit some darkening even before the microstructure is formed. Figure 34 also already indicated such behavior as the spectrum corresponding to irradiation at $F_0=0.6$ J/cm² shows a slight decrease in transmittance compared to that of the pristine material. This could be due to the fact that randomly distributed physical defects are being generated by the irradiation that locally enhance the optical field. Nagilhou et al. (2015) [63] recently presented data that supports that notion for poly(styrene) in their extension of the defect model [62]. However, the fact that this phenomenon was only observed on some of the polymers and that it was accompanied with some sort of coloration could also indicate that photochemical reactions are taking place. For λ =275 nm, polymers with a cut-off wavelength larger than λ (values can be found in Table 6) had negligible transmittance and reflectance at all fluences since they absorb almost all of the incoming light at this wavelength. The two exceptions, LDPE and PLA, are still transparent to the machining wavelength before irradiation. However, this transparency is quickly lost when the material is ablated.



Figure 35: Transmittance and reflectance at the machining wavelength λ for a) λ =800 nm and b) λ =275 nm.

In conclusion, UV-VIS data strongly suggests that a shift in optical properties, namely an increase in absorption, occurs during machining This is expected to have an impact on the threshold fluence, the magnitude of which was recently observed to have a significant effect on microstructure formation [94]. Accordingly, we determined the single pulse threshold fluences and incubation coefficients of all materials at both wavelengths using the method described in section 4.3.2.

4.4.3 Single pulse threshold fluence and incubation coefficient:

Figure 36 exemplarily describes the evolution of ablation depth at different pulse numbers and fluences for PLA at λ =800 nm.



Figure 36: Ablation depth per pulse for PLA at λ =800 nm with corresponding α at each PPS for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and four-photon absorption models. Error bars represent the standard deviation of three measurements.

As can be seen in Figure 36a, the depth-per-pulse data for multi-pulse ablation is in good agreement with equation 27. Furthermore, a clear decrease in slope is observed with increasing *PPS* numbers, which corresponds to an increase in the effective absorption coefficient. The same behavior was observed for all six polymers. This is further indication that, in addition to lowering the threshold fluence, incubation effects related to machining at higher *PPS* numbers alter a polymer's optical properties. Such behavior has been reported for fs laser ablation of

semiconductors such as fused silica [59] and polymers such as PMMA [58]. Incubation effects are believed to originate from physical and/or chemical defects that are generated by laser irradiation [1]. The exact nature and formation mechanism of these defects is still under debate and several mechanisms have been proposed such as the enhanced energy coupling efficiency due to laser-induced surface plasmons [69] and the accumulation of defect sites due to the excitation and generation of conduction-band electrons in dielectrics [68]. For the specific case of fs laser ablation of polymers, Baudach et al. (2001) observed that materials with ester bonds showcased higher incubation effects, which they suggested might be due to preferential bond breaking [70].

On the other hand, single-pulse ablation data did not provide a good fit for any of the transparent films as illustrated for PLA in Figure 36b. As can be seen, the ablation depth does not seem to follow the linear absorption model described by equation 27 (light green dotted line) as it seems to plateau at high fluence. This is unsurprising since this model is derived from the Beer-Lambert law for linearly absorbing materials. Transparent materials have a large bandgap energy that is typically larger than the energy of a photon emitted at an 800 nm wavelength and thus multiphoton absorption models are better adapted to describe their ablation behavior. Despite that fact, depth vs. fluence data for most polymers have been reported to follow a linear relationship of the same type as equation 27 with the non-linear optical effects being included in the coefficient α_{eff} [10]. This has also been observed for our multi-pulse results (Figure 36a). For the sake of comparison, the single pulse ablation data was fit to a multiphoton ablation model based on the work of Preuss et al. (1993) [79]. The model is described by the equation below:

$$d = \frac{\tau^{m-1}}{(m-1)\alpha_m} \left(\frac{1}{F_{th}^{m-1}} - \frac{1}{F_0^{m-1}}\right)$$
(29)

where *m* represents the order of photon ablation and α_m the corresponding absorption coefficient. In equation 29, all of the absorption processes of order lower than *m* are ignored. For PLA, the best fit was obtained for a four-photon absorption model (*m*=4). Through UV-VIS spectrometry, the cut-off wavelength λ_c was measured to be 235 nm for PLA, which corresponds to an optical bandgap energy of E_g =5.28 eV. Considering that a photon at a wavelength of 800 nm has a photon energy of E_p =1.55 eV, then at least four photons are required to be absorbed simultaneously in order to cross the optical bandgap of the material. Thus, the use of a four-photon absorption model is justified. Table 6 summarizes the parameters obtained from the different model fits for all polymers at both 800 nm and 275 nm.

	F _{th}	(1)	ş	2	т	for	α_m for	PPS=1	a _{eff} for 1	<i>PPS</i> =200	2 ()
	(J/c	m ²)	Ę		PPS=1		(cm ^{2m-3} /W ^{m-1})		(cm ⁻¹)		λ_{c} (nm)
λ (nm)	800	275	800	275	800	275	800	275	800	275	
LDPE	1.79	1.27	0.70	0.72	4	2	3.1 x 10 ⁻³⁵	1.1 x 10 ⁻¹¹	7.0x 10 ⁴	$8.7 \ge 10^4$	205
PC	1.72	0.31	0.73	0.92	3	1	8.7 x 10 ⁻²⁴	$7.0 \ge 10^4$	4.2 x 10 ⁴	$7.4 \ge 10^4$	281
PET	2.07	0.30	0.65	0.87	3	1	9.2 x 10 ⁻²⁴	$8.7 \ge 10^4$	4.9 x 10 ⁴	$1.1 \ge 10^5$	314
PLA	2.08	1.02	0.61	0.63	4	2	7.4 x 10 ⁻³⁶	2.1 x 10 ⁻¹²	8.1 x 10 ⁴	$8.7 \ge 10^4$	235
PMMA	2.51	0.52	0.71	0.89	3	1	3.6 x 10 ⁻²⁴	$3.2 \ge 10^4$	3.6 x 10 ⁴	$6.8 \ge 10^4$	380
PTFE	2.25	1.02	0.84	0.86	1	1	1.2 x 10 ⁴	$1.4 \ge 10^4$	2.6 x 10 ⁴	$6.7 \ge 10^4$	NA*

Table 6: Comparison of best fit model parameters at λ =800 nm and λ =275 nm.

*No λ_c value is listed for PTFE since, unlike the other films, its transmittance spectrum did not exhibit a sharp increase at a certain wavelength.

Operating at 800 nm, the only polymer that did not exhibit a multiphoton absorption behavior for single pulse ablation is PTFE (which was the only non-transparent polymer). It also displayed the lowest increase in effective absorption coefficient between *PPS*=1 and *PPS*=200 and the largest incubation coefficient. For the other five polymers, the multiphoton ablation model provided the best fit with the value of *m* being in agreement with their respective λ_c values. Therefore, the predominance of multiphoton absorption processes for single pulse ablation of transparent polymers is confirmed. However, all of them also experienced a transition to a linear absorption behavior at higher *PPS* accompanied by a very large increase in α_{eff} . The results at 275 nm were significantly different. First of all, all polymers underwent a large decrease in single pulse threshold fluence owing to the increased photon energies at this wavelength. PLA and LDPE, who have a λ_c that was even lower than 275 nm, still displayed a multiphoton absorption behavior with very low single pulse absorption. They also experienced a very slight increase in incubation coefficient that, nevertheless, remained relatively low. On the other hand, data for PC, PET, and PMMA followed the linear absorption model even for single-pulse ablation. Consequently, they displayed high absorption even at lower pulse numbers and no transition in their absorption behavior at higher pulse numbers. Coincidentally, they all experienced a large increase in incubation coefficient which means they were much less affected by increasing pulse numbers at 275 nm than at 800 nm. In conclusion, this is in agreement with the previous UV-VIS results and clearly indicates that a transition from a multiphoton to a linear absorption behavior is the main contributor to incubation effects in polymers. Therefore, the multiphoton absorption model is only valid for single or low pulse numbers since, as soon as some microstructure is formed, it will linearly absorb the subsequent pulses.

Using this data, the threshold fluence at operating conditions (*PPS*=55) for each material was calculated at both wavelengths using equation 28 and summarized in Table 7.

Material	F_{th} (55) (J/cm ²) at λ =800 nm	F_{th} (55) (J/cm ²) at λ =275 nm
LDPE	0.54	0.41
PC	0.59	0.23
PET	0.51	0.18
PLA	0.45	0.23
PMMA	0.79	0.34
PTFE	1.18	0.58

Table 7: Threshold fluences at operating conditions.

By looking at the threshold fluence values for operation at 275 nm, it can be seen that LDPE and PTFE, which were the only two polymers to retain the porous structure at this wavelength (as seen from Figure 33), had the largest F_{th} values. PMMA had the third largest threshold value and exhibited a small degree of porosity as well. On the other hand, all other materials exhibited significantly lower threshold values. Therefore, as our previous work suggests, porous laser-induced structure formation appears to be linked to the ablation threshold at the operating *PPS* number. PMMA is the polymer that is most commonly reported as observing laser-induced porosity. As first suggested by Effhimiopoulos et al. (2000), this type of morphology could be attributed to an explosive boiling mechanism [162]. In laser ablation, the incoming energy is absorbed on a ps time scale and a layer of material is removed by ionization. Depending on the

pulse duration, the underlying layers get heated to certain extent and form a hydrodynamic melt layer that re-solidifies in the order of nanoseconds [92]. For ultrashort laser machining, rapid adiabatic expansion and quasi-isochoric heating can lead to superheating of the melt volume and homogeneous bubble formation which is termed as explosive boiling [93]. Baudach et al, (2000) [15] suggest that the porosity observed at the bottom and sidewalls of fs laser ablated PMMA features are due to trapped bubbles in the re-solidifying melt layer. This notion was reinforced by numerical simulations performed by Guay et al. (2013) [13]. Assuming that our observed laserinduced microstructures are formed through a similar mechanism, the dependence on the threshold fluence at operating conditions might then be explained. As observed in Figure 37, during fs laser machining, the portion of the fluence profile of the incoming Gaussian pulses that is above the threshold fluence value of the polymer will lead to the ablation of the outermost layers. The underlying layers, that are only exposed to fluences up to F_{th} , will undergo melting. The degree of superheating of this melt layer depends on the magnitude of the fluence to which it is exposed. It is therefore also dependent on F_{th} , which is equivalent to the highest fluence a material can withstand without undergoing ionization. Therefore, the higher F_{th} is, the larger the degree of superheating of the melt layer. If the critical temperature for explosive boiling T_c is not reached, which is the case for polymers with a low F_{th} value, bubble formation will therefore not occur. Finally, Figure 38 represents the microstructure observed on LDPE for λ =275 nm at a fluence just above the threshold value ($F_0=0.45 \text{ J/cm}^2$). As can be seen, the outermost layer is getting peeled off due to the emerging pores. This is in line with the explosive boiling mechanism as the rising bubbles would coalesce near the outermost re-solidifying layer and cause compressive stresses leading to material ejection through spallation [32].



Figure 37: Effect of threshold fluence on temperature of the re-solidifying melt layer.



Figure 38: Spallation on LDPE machined at F₀=0.45 J/cm² and λ =275 nm. Scale bar represents 10 μ m.

In summary, the fits of the different absorption models confirm the large changes in optical properties that were measured by UV-VIS spectrometry. These changes heavily affect polymer machinability and the type of laser-induced structures that can appear on their surface. While the formation of a re-solidified melt layer and the accompanying increase in roughness can partly explain the observed increases in absorption and reflectance, it does not explain the surface darkening observed on LDPE, PC, and PET. Thus, as a final step, XPS analysis was performed on all samples to check if initial surface chemistry and photochemical reactions contribute to any of the aforementioned phenomena.

4.4.4 Chemical characterization:

The chemical composition and bonding structure were measured for all structures at both wavelengths. The elemental composition of all samples initially only contains carbon, oxygen, and hydrogen with the exception of PTFE, which is composed of a 2:1 fluorine-to-carbon mixture. Figure 39 presents the changes in composition as a function of fluence by displaying the atomic percentage of oxygen. These measurements omit hydrogen since it is undetectable by XPS analysis. On the other hand, Figure 40 summarizes the evolution of the bonding structure behavior of all six materials by comparing the high resolution C1s spectra for the non-modified material and a patch machined at high fluence (F_0 =7.2 J/cm²) at each wavelength. Lower values were chosen for PLA (F_0 =3.3 J/cm²) and PMMA (F_0 =5.8 J/cm²) because they underwent full ablation through the film at higher fluences.



Figure 39: Evolution of oxygen content as a function of fluence for machining at a) λ =800 nm and b) λ =275 nm. Fewer data points were collected for PMMA and PLA because, at higher fluence, the entirety of the film was ablated.

Considering Figures 39 and 40, four out of the six polymers seem to undergo photochemical reactions during machining. Indeed, for LDPE, PC, PET, and, to a lesser extent, PTFE, a dependence of surface oxygen content on fluence can be observed at both wavelengths (Figure 39). Firstly, we note that, with the exception of PTFE, this group of polymers experiences an increase in oxygen content below ablation threshold (F_0 =0.6 J/cm²) at λ =800 nm. Looking back at Figure 32, this coincides with a color change even if no microstructure is formed. However, the oxygen content drops down close to its original value once ablation process leaving behind the porous structure. Beyond the ablation threshold (F_0 >1.3 J/cm²), all four polymers once again experience an increase of surface oxygen content and increasing surface darkening with fluence at both wavelengths. The only exception being PC at λ =800 nm that actually experiences an overall decrease in oxygen which might be due to the observed degradation of its microstructure (Figure 32). The fact that PTFE did not go through similar changes in color could be due to the fact that its chemical structure changed only slightly (Figure 39). In conclusion, color change after fs laser micromachining seems to be related to surface oxidization.



Figure 40: High resolution C1s spectra for non-modified polymers (left) and machined at high fluence ($F_0=7.2 \text{ J/cm}^2$) for $\lambda=800 \text{ nm}$ (middle) and $\lambda=275 \text{ nm}$ (right). Lower values were chosen for PLA ($F_0=3.3 \text{ J/cm}^2$) and PMMA ($F_0=5.8 \text{ J/cm}^2$) because they underwent full ablation through the film at higher fluences. Both measured data (square dots) and individual labeled peak fits (solid lines) are shown.

Further insight into the mechanisms behind these chemical changes can be obtained by analyzing the changes in bonding structure after machining for each of the concerned polymers (Figure 40). For LDPE, PC, PET, and PTFE, the observed increase in oxygen content (Figure 39) is reflected in their high resolution C1s scans. At λ =800 nm, for all four polymers, either the relative amount of oxidized carbon increased at the expense of hydrocarbon bonds (PET), or new carbon oxygen peaks have appeared (LDPE, PC, and PTFE). In addition, the same type of oxidation was observed for λ =275 nm. However, it was much more pronounced at this wavelength as the oxidation peaks were significantly larger. Indeed, the proportion of carbon-oxygen bonds with respect to total carbon bonds (calculated from the area of the fitted peaks) increased from 28% to 37% for LDPE, 8% to 10% for PTFE, 21% to 26% for PET, and from 20% to 26% for PC. The dependence of the magnitude of the oxidation process on wavelength can be explained by considering photo-oxidative mechanisms prominent under ultraviolet irradiation.

Indeed, polymers are known to undergo photo-oxidative degradation when subjected to a UV light source which is generally accompanied by the appearance of a yellow color. The general mechanism of these reactions has been widely studied and they are known to produce several oxygen containing functional groups such as aldehydes, ketones and carboxylic acids [163]. Oxidation is typically initiated by free radical formation and reaction with atmospheric oxygen. Many internal chromophoric groups can act as initiator sites such as impurities, unsaturated carbon, tertiary carbon, and carbonyl groups among others [164]. The changes in bonding structure observed in Figure 40 are consistent with the established mechanisms for LDPE [165] and PET [166]. In the case of the former, initiation occurs by peroxy radical formation and subsequent chain scission and results in both aldehyde and carboxylic functional group formation. On the other hand, PET undergoes hydroperoxide formation and subsequent chain scission and results in an increase in carboxylic group formation. In the case of PC, the behavior at λ =275 nm can be explained by a photooxidative process via hydroperoxide formation and reaction with oxygen [167]. However, this does not explain the net decrease in oxygen at high fluence (Figure 39) and the decrease of the carbonate peak when irradiating PC at λ =800 nm (Figure 40) that are concurrent with the appearance of a black color (Figure 32). One reaction that could explain this is the hydrolysis of the carbonate group that is ejected as carbon dioxide by reaction with atmospheric water vapor. The detailed mechanism of PC's reaction with water can be found in Pan et al.'s (2009) study [168]. In contrast to these three polymers, PTFE is not known to typically undergo photooxidation. However, Golub et al. (1991) observed a peak similar to the one in Figure 40 on a PTFE surface treated with oxygen plasma [169]. The authors attributed this peak to oxidized carbon and hydrocarbon contamination. In summary, the high resolution XPS scans suggest that photo-oxidative mechanisms are behind the increase in oxygen content observed after machining.

Since photo-oxidation typically occurs on polymers during UV irradiation due to their high absorption at these wavelengths, it is unsurprising that such reactions were observed to take place when operating at λ =275 nm. However, the same type of reaction also occurred at λ =800 nm, which demonstrates that the microstructure formed beyond the ablation threshold is absorbent to this wavelength unlike the base material. This once again reinforces the notion of a large increase in absorption after machining as already demonstrated in the UV-VIS analysis (Figure 35) and the absorption model fits (Table 6).

Finally, the two remaining polymers (PLA and PMMA) showed no change in composition or bonding structure as a function of fluence. For both materials, the peaks retain the same proportions throughout the tested machining conditions at both wavelengths. This behavior can be explained for PMMA since it is known for its outstanding resistance to photo-oxidation as it does not contain internal chromophoric groups that could initiate free radical formation [156]. Furthermore, it is generally produced at extremely high purities which rules out any impurityinduced chromophores. On the other hand, PLA's lack of reactivity can be attributed to its extreme susceptibility to thermal degradation [170]. Jia et al. (2015) have similarly shown that femtosecond laser micromachining of PLA is a non-oxidative process as thermal degradation was observed instead [50].

In conclusion, XPS analysis has shown that polymers that are susceptible to photooxidation will experience an increase in surface oxygen content after machining. This leads to a darkening of the surface and increase in absorption that increases with operating fluence. In addition, these reactions are not limited to UV ablation as the same type of reaction is observed for λ =800 nm which we attribute to the much larger absorption of the induced microstructure with respect to this wavelength when compared the non-modified material. Therefore, irrespective of the machining wavelength, photo-oxidative reactions need to be taken into account when considering the final properties of laser induced microstructures that appear after femtosecond laser micromachining of polymers.

4.5 Conclusion

In this study, we optically and chemically characterized the femtosecond laser-induced microstructures that appear on several polymers at different operating fluences and at two separate wavelengths. At λ =800 nm, all polymers formed a porous structure. In addition, LDPE, PET, and PC showed a darkening of their surface at higher fluences. At λ =275 nm, only PTFE and LDPE retained the porous structure, while the other polymers mostly experienced melt formation. This was attributed to the threshold fluence of these two polymers that was still high enough at this wavelength for explosive boiling to occur. The magnitude of the threshold fluence was further determined to be dependent on the changes in optical properties that occur during machining. UV-VIS spectrometry showed that an increase in absorption and reflectance occurred when the laserinduced microstructures were formed. In addition, LDPE, PET and PC, were observed to be increasingly absorbent as fluence increased. Fitting of different absorption models confirmed the observed increases in absorption. Furthermore, it revealed that a transition from a multiphoton absorption behavior during single pulse ablation to linear absorption at higher pulse numbers was occurring for transparent polymers. This shift was identified as being the main contributor to incubation effects. It is therefore crucial in determining the threshold fluence when operating at high pulse numbers. Finally, XPS analysis revealed that photo-oxidative mechanisms are behind the darkening and continuous increase in absorption observed on LDPE, PC, and PET. In conclusion, we identified the main parameters that lead to porous structure formation on polymer surfaces as well as the optical and chemical processes that affect them.

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Conflicts of interest

The authors declare no conflict of interest.

Chapter 5 Femtosecond Laser-Induced Porosity on Poly(ethylene) Surfaces – a Crystallographic and Rheological study

5.1 Preface

The results from our previous study suggested that femtosecond laser-induced porosity forms as a consequence of explosive boiling. In this chapter, experimental evidence of explosive boiling was sought out in order to confirm this hypothesis. A crystallographic study by grazing incidence X-ray diffractomery was performed on pristine and machined HDPE in order to assess if fs laser-induced structures are formed from a re-solidified melt. Also, since the viscoelastic properties of a melt affect the rate of bubble growth within it, several PE grades with increasing molecular weight were rheologically characterized and then machined. Thus, the viscoelastic parameters that affect pore dimension were identified which will allow future optimization of fs laser-induced porous structures. This chapter is a reproduction of an article published in the Journal of Applied Physics. Supplementary data for this study can be found in Appendix C. It contains the small angle oscillatory shear curves not shown in this chapter. The complete citation of the published article is:

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Femtosecond Laser-Induced Porosity on Poly(ethylene) Surfaces – a Crystallographic and Rheological study

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Abstract

In recent years, femtosecond (fs) laser irradiation of polymer surfaces has been shown to produce novel porous topologies that present a multi-scale roughness. In our study, grazing incidence x-ray diffractometry (GIXRD) results showed the appearance of a monoclinic crystalline phase on fs laser machined high density polyethylene (HDPE) which is a deformation of the orthorhombic phase typically observed in pristine HDPE. This was accompanied with a local decrease in crystallinity. These findings confirmed that the induced porosity was a consequence of the rapid quenching of a superheated melt layer undergoing phase explosion. In addition, several poly(ethylene) samples with different average molecular weights were machined under the same conditions. Scanning electron micrography, along with small angle oscillatory shear tests, indicated that final pore size decreases with increasing average molecular weight or increasing melt viscosity since these parameters act against bubble growth during phase explosion. In addition, through computed tomography, the internal structure of the porous layer was investigated. Through this technique, the average pore size and pore size distribution can be computed by chord length analysis. In conclusion, in this study, the mechanisms behind the formation of femtosecond laser-induced porous structures and the parameters that control their dimensions have been established.

5.2 Introduction

Polymer surfaces have traditionally been difficult to process by laser machining due to their low absorption [171]. With the advent of femtosecond (fs) technology, polymer machining is now possible through non-linear optical processes such as multiphoton absorption [172]. This now allows the inscription of precise micrometric geometries on polymer surfaces. Precise ablation has allowed the fabrication of polymeric surfaces for lab-on-chip applications [118], Fresnel lenses [120], and intraocular lenses [128] among others. In contrast with such laser inscribed structures, femtosecond laser-induced (or self-assembled) microstructures have recently been of interest. Indeed, fs irradiation is known to produce a multiscale micro/nano roughness on several types of materials which is advantageous for the manipulation of their wettability [3, 110, 173, 174]. In the case of polymers, the structure that has been most commonly reported is fs laser-induced porosity. This phenomenon was initially observed on the side walls of inscribed lines and holes on poly(methyl methacrylate) (PMMA) and poly(carbonate) (PC) [16, 70]. Since then, homogeneous polymer irradiation under certain conditions has been shown to cause the formation of a porous microstructure over the whole surface [3, 40, 96]. The resulting increase in surface area can be greatly beneficial for a number of applications such as omniphobic materials [96] or biomedical implants [175]. For example, Castillejo et al. have reported preferential fibroblast attachment and growth on a fs laser-induced porous structure produced on chitosan and starch [176]. Similar results for fibroblast cells were also reported by Daskalova et al. on porous structures produced by fs laser machining on collagen, gelatin, and elastin [177]. However, not much is known regarding the mechanism behind the formation of fs laser-induced porous structures which limits their optimization for specific applications.

So far, several authors have hypothesized that the porous topology forms as a consequence of explosive boiling. This phenomenon, also termed as phase explosion, occurs in the melt layer that forms beneath the ionized material during the ablation process. If the laser fluence is sufficiently high and the pulse duration sufficiently short, this melt layer can theoretically heat up above a certain critical temperature T_c where homogeneous bubble formation occurs [93]. Effthimiopoulos et al.'s study was the first to suggest that the porosity induced on PMMA after irradiation is related to the bubble formation during boiling [162]. Baudach et al. later suggested that the side wall porosity they observed in ablated craters on PMMA and PC are due to the same mechanism [15]. The theoretical plausibility of this hypothesis on PMMA was also validated by the numerical simulations performed by Guay et al. [13]. In our previous work, we further suggested that this phenomenon can occur on any polymer as long as its threshold fluence is large enough so that the melt layer is heated past T_c [40]. In summary, during femtosecond laser polymer ablation, energy delivery to the surface and subsequent boiling happens in the order of picoseconds [92]. The high rate of heating leads to the formation of a melt layer that is almost immediately quenched to room temperature between two consecutive pulses. The melt thus re-solidifies in the shape of a porous layer with the pores being a remnant of the volume occupied by the bubbles during phase explosion. While this theory seems to be generally accepted today, the timescale involved in the formation of these structures is too short to visualize the process directly. Thus, experimental evidence of melt re-solidification needs to be retroactively measured from a change in surface properties. In crystalline polymers, rapid melt and quenching should have an effect on the crystallinity and/or crystal structure since the high cooling rate limits the time available for crystal formation and growth. The only measurements on the effect of femtosecond laser irradiation on polymer crystallinity were performed on amorphous PLA where, as expected, crystallinity was not induced during machining [50, 178].

Another relatively unexplored aspect related to these microstructures is the dimension of the pore size. If it is indeed related to bubble growth during boiling, then pore size should inevitably be related to the viscoelastic properties of the melt layer. Rebollar et al. have previously observed that the size of surface swelling bubbles after nanosecond laser irradiation of PMMA is inversely proportional to average molecular weight M_w [179]. They explained this correlation by stating that polymers with lower M_w are less viscous when melted and offer more free volume. This would promote bubble growth to larger sizes. So far, no other study reported this phenomenon and it is unclear if the same phenomenon applies to laser-induced porous structures on polymer surfaces. Another parameter that could affect pore size is the laser fluence. In their study on PMMA, Baset et al. suggest that the porosity observed on the bottom or side walls of ablated craters depends on the incoming laser power [16]. With increasing power, more pores were observed to appear but their size diminished. In our two recent studies, the effect of fluence on laser-induced microstructure on several polymers was investigated [40, 94]. While some polymers had their texture affected at high fluence, pore size was observed to be mostly unaffected by this
parameter. The reason behind this discrepancy could be attributed to the very high accumulated fluence values achieved when producing laser-induced structures over a large area, as opposed to crater inscription.

Finally, the quantification of femtosecond laser induced porosity remains a challenge for several reasons. First of all, the previously mentioned studies all report pore sizes of up to a few μ m at most. Furthermore, this microstructure is typically less than 50 μ m thick [94, 96] and rests atop the bulk non-modified polymer. This renders techniques such as porosimetry inapplicable since it would be nearly impossible to separate the modified surface layer from the non-modified bulk. In addition, there is no evidence that the pores are interconnected. As a consequence, even if the surface layer were to be somehow separated from the bulk, any intrusive technique would ignore pores formed within the volume of the structure. Thus, a method to adequately quantify femtosecond laser induced porosity is still lacking.

In this study, the effect of femtosecond laser machining on the crystallinity and crystallographic structure of high density poly(ethylene) (HDPE) is studied. In addition, six different poly(ethylene) (PE) samples with increasing M_w and different melt viscosities were machined to see if pore size is indeed correlated to these properties. The internal structure of the porous layer formed after machining was also investigated by computed tomography. These experiments will therefore greatly contribute to our understanding of the formation of femtosecond laser induced microstructures thus allowing future pore size optimization for specific applications.

5.3 Materials and methods

5.3.1 Materials:

Seven different grades of poly(ethylene) were used in this study. For GIXRD, 4*4 cm square samples were cut from a 1.5 mm thick HDPE sheet (Grade 1) purchased from McMaster-Carr. For this particular measurement, a poly(ethylene) grade with high density was chosen because of its high crystallinity which makes changes to its crystallographic structure easily detectable. Measurements were done on two samples: a non-modified pristine sample and a laser machined sample. They will be referred to as 1-P and 1-L respectively.

For all other experiments, six PE grades with increasing average molecular weights were used. Samples were compression molded from pellets or powders (Sigma Aldrich) into 2.54 cm diameter discs with 1 mm thickness at 150°C and 5 metric tonnes of pressure for 15 minutes. Table 8 presents the properties of the six PE grades used for these experiments as well as the sample number assigned to them. Weight average molecular weights M_w were measured by GPC as described in section 5.3.5 and density values ρ were provided by the supplier. The M_w range for the ultra high molecular weight (UHMW) sample was also provided by the supplier because its viscosity lied outside the measurement range of the HT-GPC setup used.

M_w (kg/mol)	ρ (g/cm ³)	
5	0.92	
9	0.94	
39	0.906	
55	0.925	
59	0.952	
3x10 ³ -6x10 ³	0.94	
	<i>M</i> _w (kg/mol) 5 9 39 55 59 3x10 ³ -6x10 ³	

Table 8: Densities and weight average molecular weights of PE grades used for rheometry experiments.

5.3.2 Laser micromachining:

A solid state Ti:sapphire laser system (Coherent Libra) delivering a Gaussian beam at a wavelength of 800 nm and in pulses of 150 fs duration operated at a repetition rate f_p of 1 kHz was used for all micromachining experiments. The 4 W beam passes through a digitally controlled attenuator consisting of a half-wave plate and a polarizing beam splitter in order to lower its power down to the desired value *P*. It then passes through a digitally controlled mechanical shutter (Uniblitz) before being focused onto the sample through a 100 mm lens down to a 44 µm spot size ω_0 . The sample rests atop a 3D stage (Newport Corporation) whose trajectory and velocity *v* are controlled by the GOL3D software (GBC&S). All laser-induced microstructures were produced by raster scanning the beam with a spatial overlap Φ of 0.95, a pulse-per-spot number *PPS* of 55, and a single pulse peak fluence F_0 of 3.3 J/cm². F_0 and *PPS* were calculated from processing parameters using the following equations:

$$F_0 = \frac{8P}{\pi\omega_0^2 f_p} \tag{30}$$

$$PPS = \frac{\omega_0 f_p}{\nu(1-\Phi)} \tag{31}$$

5.3.3 Scanning electron microscopy:

All samples were cleaned in a sonication ethanol bath for 5 mins immediately after machining in order to get rid of any loose machining debris. The surface structure was imaged by a scanning electron microscope (SEM) (FEI Inspect F50). This involved sputter coating (SPI-Module, Structure Probe Inc.) the samples with a 10 nm layer of gold in order to avoid surface charging.

5.3.4 Grazing incidence x-ray diffraction (GIXRD):

GIXRD scans were performed using a Bruker D8 Discovery diffractometer equipped with a Cu-K α source (λ =0.154 nm) and a HiSTAR area detector. A depth profile of the samples was performed by varying the incident angle θ from 10° to 0.2° in order to vary the penetration depth of the x-ray beam. This way, the crystallographic structure of the bulk and modified surface layer can be compared. A 15 min step-scan in increments of 0.02° 2 θ over a 1*1 mm area of the sample was performed at each incident angle. Crystallinity was determined by calculating the relative area of the crystalline peaks and amorphous background with respect to the total area under the intensity curve.

5.3.5 Gel permeation chromatography:

The average molecular weights M_w of grades 2 to 7 were determined using a Viscotek 350 (Malvern Panalytical) high temperature gel permeation chromatography (HT-GPC) setup equipped with 3 PLgel mixed organic columns (Agilent). Calibration was performed using a broad molecular weight range polystyrene standard kit (Scientific Polymer Products, Inc.). Each sample was dissolved in trichlorobenzene (containing 500 ppm of butylatedhydroxytoluene) at a concentration of 2 mg/mL. The measurements were performed at 140°C using a 200 µL injection volume and a flowrate of 1 mL/min.

5.3.6 Rheometry:

All measurements were performed using a strain-controlled Anton-Paar MCR 302 rheometer set up with a parallel plate stainless steel accessory (25 mm diameter) and a CTD 450

convection oven heated to 190°C. For each sample, both an oscillatory shear test and a ramping rotational shear test were performed. For the oscillatory measurements, a preliminary amplitude sweep was performed on all samples from 0.01% to 100% strain amplitude γ_0 . As a consequence, all experiments were performed at a strain amplitude of 1% as the value falls within the viscoelastic range for all samples. Subsequently, a frequency sweep, where the angular frequency ω was varied from 0.3 to 300 rad/s, was performed on all samples in order to measure the storage and loss moduli *G*' and *G*'' as well as the complex viscosity η^* . For the ramping measurements, the dynamic viscosity η was measured while increasing the strain rate γ from 0.01 to 100 s⁻¹.

5.3.7 Computed tomography:

Computed tomography (CT) was performed using an Xradia 520 Versa (Zeiss) with a spatial resolution of 0.7 μ m. 3D reconstruction and slicing was performed using the Dragonfly software (Object Research Systems). The porosity was calculated by the software by measuring the volume ratio of pore voxels to total (pore and solid) voxels, For the calculation of pore size distribution, 10 slices separated by a distance of 1 μ m were analyzed. They were first thresholded using Yen's algorithm in order to separate them into black (pores) and white (solid) pixels [180]. Each slice was then both horizontally and vertically scanned and the chord length of the pores (number of consecutive black pixels) was calculated using a Matlab (MathWorks) code.

5.4 Results and discussion

First, a comparison between the crystal structure of non-modified and laser machined HDPE was performed in order to look for evidence of melt resolidification and thus validate the hypothesis that explosive boiling is the mechanism responsible for the resulting porous structures. Subsequently, the effect of increasing molecular weight on laser-induced pore size and the internal structure of the modified surface layer were investigated. Finally, the results were explained by measuring the change in viscoelastic properties with increasing molecular weight through rheometry analysis and evaluating how it would affect explosive boiling during laser machining.

5.4.1 Effect of laser machining on crystal structure:

Figure 41 shows the micrographs for non-modified (1-P) and laser machined (1-L) HDPE, while Figure 42 represents the resulting large incident angle GIXRD scans.





Figure 41: SEM micrographs for samples a) 1-P and b) 1-L.



Figure 42: GIXRD scans for large incident angles on samples a) 1-P and b) 1-L.

Looking at Figure 42a, it is apparent that our HDPE sample is semi-crystalline as seen from the presence of two sharp peaks. The signals strongly indicate that the crystalline region is arranged in the typical orthorhombic structure with *Pnam* spacing that is characteristic of HDPE (Figure 44a) [181]. Thus, the large peak at 1.53 Å⁻¹ corresponds to the reflection from the [110] plane, while the smaller peak at 1.69 Å⁻¹ corresponds to the reflection from the [200] plane [182, 183]. By comparing the results from sample 1-P (Figure 42a) to those from sample 1-L (Figure 42b), it

is evident that the results are almost identical. This is in contrast with the results from scans at low incident angles as illustrated in Figure 43.



Figure 43: GIXRD scans for small incident angles on samples a) 1-P and b) 1-L.

Figure 43a shows no difference in crystallographic structure for sample 1-P between the scans at low and high incident angles. This indicates that the HDPE in question has a relatively homogeneous crystalline structure throughout its depth profile, even in the first few layers underneath the surface. On the other hand, Figure 43b clearly indicates that, for sample 1-L, new peaks can be identified for incidence angles below 1.5°. For an incident angle of 0.8°, the [110] and [200] reflections of the orthorhombic structure are still present. However, three new peaks appear located at 1.47 Å⁻¹, 1.6 Å⁻¹, and 1.77 Å⁻¹. As the incident angle decreases, the orthorhombic peaks gradually recede until only the three new peaks are left at 0.2°. This is a clear indication of the formation of a new crystalline phase after machining. The combination of these three peaks is consistent with the reflections from the [010], [-110], and [100] planes of a monoclinic structure with $P2_1/m$ spacing (Figure 44b) [184]. This phase is similar to the orthorhombic one except for one of the lattice vectors not being orthogonal to the other two. This distortion of the orthorhombic arrangement is only formed and stable at high temperatures and pressures (typically above 6 GPa at 280°C) and typically reverts back at room temperature [184]. It arises due to tensile or compressive stresses above the yield point of the material [185]. The ultrashort timescale of energy delivery during femtosecond laser machining has been reported to induce very high local pressures

and temperatures. For dielectrics such as silica, Hu et al. have calculated local pressures to be in the TPa range for the ionized layer [186]. In addition, Bulgakova et al. have demonstrated that the underlying melt layer will be superheated to temperatures of several thousand Kelvin and subjected to tensile stresses of several dozen MPa [187] which are conditions that can lead to homogeneous bubble formation as demonstrated by Bellouard et al. [188]. Therefore, we conclude that femtosecond laser micromachining of HDPE can lead to the conditions necessary for the formation of the monoclinic phase. However, the fact that it was still present at room temperature can only mean that the superheated melt layer was very rapidly quenched, thus preventing it from reverting to the orthorhombic phase. In order to check this hypothesis, the samples were annealed at 105°C for 24 hours to check if the orthorhombic phase would be recovered. The annealed pristine sample and annealed laser machined sample will be referred to as 1-PA and 1-LA respectively. Figure 45 presents the GIXRD results at low incidence angles for the annealed samples.



Figure 44: Top view of a) orthorhombic PE crystal with Pnam spacing and b) monoclinic PE crystal with P2₁/m spacing. Adapted from [184].



Figure 45: GIXRD scans for small incident angles on samples a) 1-PA b) 1-LA.

The results for sample 1-LA (Figure 45b) show a complete recovery of the orthorhombic phase at an incident angle of 0.8°. At θ =0.2°, the orthorhombic phase is prevalent even if a small amount of residual monoclinic phase subsides. The recovery of the original crystalline structure of the material by annealing confirms that the peak identification was correct and that femtosecond laser machining of HDPE does indeed induce the formation of a monoclinic phase. For sample 1-PA (Figure 45a), the only noticeable change is that peak intensity increases after annealing. Table 9 summarizes the crystallinity values computed from all GIXRD measurements.

<i>θ</i> (°)	1-P (% Crystallinity)	% Crystallinity) 1-PA (% Crystallinity) 1		1-LA (% Crystallinity)	
10	55	72	54	69	
4.0	54	70	53	69	
2.5	52	68	52	70	
1.5	54	71	52	68	
0.8	54	68	44	58	
0.5	52	71	46	58	
0.2	52	69	45	57	

Table 9: Effect of laser machining and annealing on crystallinity for Grade 1.

Sample 1-P's crystallinity was measured to be around 53%. For $\theta > 1.5^{\circ}$, machining did not have a significant effect on crystallinity as seen from the measurements for sample 1-L. This was expected since these measurements come from the bulk material beneath the modified layer. In the modified layer ($\theta < 1.5^{\circ}$), the average crystallinity dropped to 45%. This means that, despite the appearance of a new crystalline phase, the polymer became more amorphous overall. This is consistent with a rapid melting and quenching mechanism. Finally, as expected, annealing increased the crystallinity for all measurements by more than 10% as observed for samples 1-PA and 1-LA.

In conclusion, GIXRD measurements confirm that the femtosecond-laser induced porous microstructures are formed from the resolidification of a rapidly quenched superheated melt. In this case, the viscoelastic properties of the melt should have a significant effect on bubble growth during boiling and thus on the final laser-induced pore size. Since the viscoelastic properties of polymer melts are dictated by their molecular weight, the effect of M_w on laser-induced porous structures was investigated next.

5.4.2 Effect of molecular weight on laser-induced porous structures:

All grades listed in Table 8 were laser machined as described in section 5.3.2. Figure 46 presents the resulting SEM micrographs.



Figure 46: Decrease in pore size with increasing average molecular weight.

By looking at the different micrographs, it is apparent that molecular weight seems to have a significant effect on laser-induced pore size. With the exception of the two grades with the lowest M_w (grades 2 and 3), increasing molecular weight from grade 4 to grade 7 seems to correlate with decreasing pore size. In order to further investigate the internal structure of such laser modified surface layers, computed tomography was performed on the femtosecond laser-induced microstructure produced on grade 4 (Figure 47).



Figure 47: a) Computed tomography 3D reconstruction of a 700*700*10 μ m³ volume located inside the laser-induced surface microstructure on grade 4 and b) 150*150 μ m² thresholded area with example measurements of horizontal chord length l_{cx} and vertical chord length l_{cy}.

As can be seen in the 3D reconstruction, computed tomography successfully recreated the internal structure of the laser modified surface layer. By comparing solid voxel volume to total volume, the porosity can be calculated with the value for the particular volume shown in Figure 47 being 55%. Furthermore, the reconstruction showed that most of the pores are interconnected within the microstructure. Thus, traditional pore size analysis is not possible and we resorted to chord length measurements as described in section 5.3.7 and illustrated in Figure 47b. Figure 48 exemplarily presents chord length distributions for the horizontal and vertical directions for the volume shown in Figure 47.



Figure 48: a) Horizontal and b) vertical chord length distributions for the laser induced structure produced on grade 4.

By comparing Figure 48a and 48b, the horizontal and vertical chord length distributions appear to be similar with most lengths falling in between 2 and 4 μ m. Thus, the pores can be said to have similar sizes and seem to be homogeneously distributed throughout the modified volume. These results can only be explained by evaluating how M_w affects the viscoelastic melt properties and therewith bubble growth during femtosecond laser-induced explosive boiling. Thus, as a final step, the viscoelastic properties of the samples in question were measured by rheometry analysis.

5.4.3 Effect of viscoelastic properties on laser-induced pore size:

Figure 49 presents the viscosity results from both the oscillatory and ramping shear tests on all grades listed in Table 8. Since all measurements were taken at a temperature of 190°C, they cannot be used to quantitatively describe melt flow behavior during femtosecond laser machining. Indeed, as previously mentioned, the temperatures reached during machining can be an order of magnitude higher, which would lead to much lower viscosities. However, the ranking of the six grades from least viscous to most viscous can still be used as a qualitative assessment of melt flow properties at high temperatures.



Figure 49: a) Complex viscosity versus angular frequency and b) dynamic viscosity versus shear rate at 190°C.

Both tests gave similar results with respect to viscosity. All grades experienced some kind of shear thinning behavior as their viscosity decreased with increasing angular frequency or shear rate. Looking back at Table 8, as expected, viscosity increased by orders of magnitude with increasing molecular M_w . Table 10 summarizes these results in addition to the G' and G'' values.

Grade number	η* (Pa·s)	η (Pa·s)	<i>G'</i> (Pa)	<i>G</i> "(Pa)
2	0.2	0.15	0.081	0.227
3	0.4	0.2	0.23	0.4
4	13	25	1.4	2.1
5	552	759	156	641
6	1100	1310	426	1240
7	123000	160000	140000	43100
5 6 7	552 1100 123000	759 1310 160000	156 426 140000	

Tabl	e 10:	Viscoelas	tic proper	ties at 190	^o C, ω=1	rad · s ⁻¹	, and $\gamma =$	1 s-	l
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In summary these grades can be grouped into three categories based on their melt viscoelastic properties: I-low viscosity grades (grades 2, 3, and 4), II-moderate viscosity grades (grades 5 and 6), and III- high viscosity grades (grade 7). By looking at the moduli, in the first

group, viscous dissipation is prevalent and there is limited resistance to flow. In contrast, grade 7 offers significant flow resistance as elastic recovery is dominant. Finally, group II offers flow properties that are somewhere in between.

If we consider bubble growth dynamics in viscoelastic melts, then the correlation between increasing M_w and decreasing pore size observed in Figure 46 can be explained. No physical model to describe bubble growth induced by the extreme heating rates achieved during femtosecond laser machining has been proposed yet. However, a qualitative description of the parameters that affect it can be made by considering homogeneous spherical bubble growth in a viscoelastic liquid. This can be described by the adapted Rayleigh-Plesset equation [189]:

$$R\frac{d^{2}R}{dt^{2}} + \frac{3}{2}\left(\frac{dR}{dt}\right)^{2} = \frac{1}{\rho_{l}}\left(P_{g} - P_{\infty}\right) - 4\frac{\eta_{l}}{R}\frac{dR}{dt} - \frac{2\gamma^{*}}{\rho_{l}R} - \frac{E_{\sigma}}{\rho_{l}}$$
(32)

Where *R* is the bubble radius, *t* is time, ρ_l is the density of the liquid, P_g is the pressure inside the bubble, P_{∞} is the external pressure, η_l is the liquid kinematic viscosity, γ^* is the surface tension of the bubble/liquid interface, and E_{σ} is the elastic stress.

Due to the number of time dependent components, solving equation 32 requires the simultaneous coupled solution of several differential equations. However, a qualitative description of the effects of the different parameters on the bubble growth rate can be made. First of all, increasing viscosity clearly decreases the rate of bubble expansion. Samples with large viscosities provide larger resistances to flow once melted compared to samples with lower viscosities. Thus, after a laser pulse hits the sample and heats the surface, the bubbles that nucleate in samples with high viscosity will grow to much smaller sizes over the heating duration when compared to bubbles nucleating in low viscosity samples. After the end of the pulse duration, once the melt gets quenched, samples where bubbles have grown to larger sizes will end up with larger voids within their volume. This explains the large decrease in pore size at high M_w (Figure 46) since this comes along with increasingly larger viscosities (Figure 49).

While surface tension is harder to evaluate and does not always correlate with molecular weight, it has been shown for poly(ethylene) that, similarly to viscosity, its value increases with increasing molecular weight [190]. The value of the elastic component E_{σ} depends on the model used to estimate it, such as the linear elastic, the neo-Hookean, or the Yang and Church model [191]. In our case, it can be estimated by the magnitude of the storage modulus G'. Like the

previously discussed properties, G' also increases with molecular weight (Table 10). In addition, its value gets closer to the loss modulus G'' with increasing M_w until eventually exceeding it for grade 7. This increase in elastic behavior at the expense of viscous dissipation at high molecular weights further explains the large decrease in pore size at high M_w . Indeed, since elastic recovery is dominant for such samples, the energy required for material deformation is much higher than for lower M_w samples. The bubbles nucleated in the laser heated melt layer thus experience an extremely large resistance to growth which leads to a small pore size.

Finally, the density of the liquid should also have an effect. Looking back at Table 8 and Figure 46, the polymer density does not correlate with pore size for high M_w values (39 kg/mol and above). However, a closer inspection of equation 32 reveals that as viscosity, surface tension, and elastic stress decrease (in other words at low M_w), the effect of ρ_l on the bubble growth rate is magnified as the pressure term of equation 32 starts to dominate. By checking the density values in Table 8, it can be seen that even though grades 2 and 3 have smaller M_w when compared to grade 4, they are also denser and thus offer less free volume according to Flory-Fox theory [192]. From this perspective, once melted, denser polymers offer less space for bubbles to grow than low density polymers and will thus end up with smaller bubbles during laser machining. This could explain why, despite their extremely low viscosity, the pores on grades 2 and 3 are smaller than those on grade 4.

In conclusion, viscoelastic melt properties have a significant effect on femtosecond laserinduced pore size on polymer surfaces. With the exception of polymers with very low molecular weights, pore size is inversely correlated with molecular weight due to the increase in forces that inhibit the bubble growth rate during explosive boiling. Thus, a good understanding of the viscoelastic properties of a polymer are crucial for the optimization of femtosecond laser-induced structures on its surface.

5.5 Conclusion

In this study, the effect of femtosecond laser machining on the crystallographic structure of HDPE was investigated. Results indicate that machining led to a local decrease in crystallinity and the appearance of a new monoclinic phase. This constitutes evidence that femtosecond laserinduced porosity is formed as a consequence of the rapid quenching of a superheated melt layer undergoing explosive boiling. Second, increasing molecular weight was observed to lead to a decrease in laser-induced pore size. Computed tomography allowed the investigation of the internal structure of the modified surface and showed that pores are interconnected and homogeneously distributed throughout the modified volume. Finally, the effect of molecular weight on pore size was explained by measuring the viscoelastic melt properties of the studied samples. At high molecular weights, the increased viscosity was determined to lead to lower bubble growth rates during explosive boiling, and thus to lower laser-induced pore sizes. By contributing to the current knowledge of the mechanisms behind the formation of femtosecond laser-induced porosity, this study will thus help the future optimization of pore size for omniphobic materials such as SLIPS or biomedical implants such as grafts and scaffolds.

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Chapter 6 Wettability modification of porous PET by atmospheric femtosecond PLD

6.1 Preface

In the previous chapters, femtosecond laser-induced porous structures were presented and their properties were characterized. By gaining a better understanding of their formation mechanism, the parameters that affect their dimensions were identified. Thus, the structure dimensions can now be optimized to target specific applications. However, even if a desired topology can be fabricated, its surface wettability will be dictated by the material properties and the machining process and will thus not necessarily match the requirements of the targeted application. Typical wettability modification techniques involve surface texturing which is inapplicable in our case since it would compromise the porous topology. Therefore, in this chapter, a novel pulsed laser deposition setup for the wettability modification of porous surfaces is presented. Hydrophilic titanium oxide nanoparticles were controllably incorporated into porous PET in order to achieve various degrees of wettability. This chapter is a reproduction of an article published in the journal Applied Surface Science. The complete citation of the published article is:

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Wettability modification of porous PET by atmospheric femtosecond PLD

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Abstract

In this study, porous structures were created on poly(ethylene terephthalate) (PET) by femtosecond (fs) laser micromachining. While such structures offer a texture that is desirable for several applications, their wettability does not always match the application in question. The aim of this investigation is to tune the wettability of such surfaces by incorporating a controlled amount of nanoparticles into the structure. The machined PET samples were thus used as substrates for fs pulsed laser deposition (PLD) of titanium under ambient conditions. The nanoparticles were deposited as nanochain clusters due to the formation of an oxide layer between individual nanoparticles. The stability of nanoparticle incorporation was tested by placing the samples in an ultrasonic ethanol bath. Results indicated that nanoparticles were still successfully incorporated into the microstructure after sonication. Nanoparticle surface coverage was observed to be controllable through the operating fluence. The dynamic contact angles of the resulting composite surface were observed to decrease with increasing titanium incorporation. Therefore, this work highlights atmospheric fs PLD as a method for wettability modification of high surface area microstructures without undermining their topology. In addition, this technique uses almost the same equipment as the machining process by which the microstructures are initially created, further highlighting its practicality.

6.2 Introduction

Polymeric materials with high surface area have recently become highly sought after materials due to their wide range of application possibilities including catalysis [193] and biomedical implant materials [175]. They are typically produced by surface modification techniques that induce porosity or a dual-scale texture [194]. Such production methods usually alter the physical and chemical properties of the surface. The resulting material will therefore exhibit specific surface properties that are not easily altered without compromising the newly created surface texture, thus limiting its versatility with regards to the application in question. Recently, we have reported on processing polymer surfaces by femtosecond (fs) laser micromachining, which results in porous surface structures that further exhibit nanoscale roughness [3]. Even if the mechanism behind the formation of these surface structures is not yet fully established, they have been observed to appear on a wide variety of polymers upon laser machining [94]. Their novel surface topography makes them prime candidates for various high surface area applications. In this study, we explore the possibility of varying one of the surface properties, namely surface wettability, on a continuous scale with minimal modification to the porous surface topography.

The wettability of a material is dictated by its surface chemistry and roughness. Therefore, wettability modification of a given surface can be achieved by tuning one or both of these properties. In the case of polymers, surface chemistry is typically altered by plasma treatment or UV irradiation by the addition of new functional groups [195]. While such techniques have been reported to successfully alter wettability, they require parameter modification on a case-by-case basis as the outcome heavily depends on the nature of the polymer in question. On the other hand, increasing surface roughness enhances the intrinsic wettability of a homogenous surface as described by the Wenzel wettability model [97].

$$\cos\theta^* = r^* \cos\theta_Y \tag{33}$$

Where θ_Y is the Young's contact angle, θ^* is the apparent contact angle, and r^* is the roughness factor. One approach for polymer roughness enhancement is to directly impart a microscale pattern onto the surface. Over the years, several techniques have been developed to that effect such as photolithogrpahy [196-198], direct laser texturing [199-201], or plasma processing [202-204]. But since fs laser machined polymers are already microtextured, any additional texturing will cause

significant damage to the high surface area topology. Therefore, the only way to enhance surface roughness without compromising the underlying microstructure is to modify it on the nanoscale through the incorporation of nanoparticles. This will in fact serve a dual purpose as not only will the added nanoparticles increase the value of the roughness factor r^* (Equation 33), but they will also induce chemical heterogeneity on the surface as their composition is different than that of the substrate. For such chemically heterogeneous surfaces, the overall wettability will also heavily depend on the relative amount of each component as described by the Cassie-Baxter wettability model for a multi-component system [98].

$$\cos\theta^* = f_1 \cos\theta_{Y_1} + f_2 \cos\theta_{Y_2} + \dots + f_i \cos\theta_{Y_i}$$
(34)

Where θ_{Y_i} is the Young's contact angle of component *i* and *f_i* is its area fraction. This implies that, if the nanoparticles offer a surface chemistry that is sufficiently distinct from the substrate material, tuneable wettability can be achieved by controlling the density of the deposited nanoparticle coverage [205]. Over the years, many techniques for nanoparticle deposition such as chemical vapour deposition and layer by layer deposition have been developed. However, they typically have complex requirements such as a highly controlled environment and separate nanoparticle generation and deposition steps [206]. Pulsed laser deposition (PLD) is a single step alternative for the simultaneous generation and deposition of nanoparticles by laser ablation of a target material which, in addition, can be performed by using the same equipment as laser micromachining.

In PLD, nanoparticles are generated by focusing an incoming beam onto a target placed in a vacuum chamber causing material ejection through ablation and plasma formation. The expanding nanoparticle plume then reaches the substrate to be coated where it condenses and deposits as a uniform thin film. Typically, operating at increased pulse numbers and high fluence increases the impinging nanoparticle flux on the substrate and promotes film formation [207]. The main drawback being that a high flux can increase sputtering damage and promote the inclusion of unwanted microscopic particulates due to melting and exfoliation of the target [208]. With the development of fs laser technology, this effect has been mitigated as the very small timescale of ultrashort pulses minimises thermal effects [209-211]. It is also critical that the nanoparticle plume reaches the substrate in order for deposition to occur. This is why PLD is typically carried out in a vacuum chamber as this minimises the resistance to plasma plume expansion and ensures a working distance in the centimetre range. The need for vacuum is considered one of the main

limitations of this technique since it limits cost-effectiveness and sustainability. Yet, a surprisingly low number of studies have attempted to overcome that. Out of the few reports studying atmospheric pressure PLD, the studies by Kononenko et al. [212] and Nedyalkov et al. [213] have successfully demonstrated film formation by working at very high pulse numbers and targetsubstrate distances in the millimetre range. Similarly, McCann et al. operated at ambient conditions by focusing a laser source through a transparent substrate which was micrometres away from the target [214]. Finally, film formation on the substrate is dominated by the nucleation rate of adsorbed nanoparticle clusters and their subsequent surface diffusion and coalescence into a uniform film [215]. In order to promote surface diffusion, PLD is usually performed on heated substrates with very smooth surfaces [216].

In this study, a porous surface structure was created on poly(ethylene terephthalate) by fs laser micromachining to later serve as a substrate for atmospheric PLD of titanium nanoparticles. While PLD has been used in the past for the deposition of films that exhibit a nanoscale structure [217], it has almost exclusively been used as a coating technique to completely cover a smooth, low surface roughness substrate with a uniform film. In our study, we aim at exploiting the high surface roughness of our substrate to actually inhibit surface diffusion and therefore promote the deposition of separate nanoparticle clusters instead of uniform film formation. This is desirable in our case since it will mitigate the possibility of completely covering the underlying porous structure. In addition, the whole process is performed under ambient pressure, thus circumventing the traditional requirement for low pressure conditions. Applying atmospheric PLD for nanoparticle deposition into high-surface area polymer surfaces is therefore highly unconventional and, to the authors' knowledge, unreported yet. One of the main advantages of this technique is that it requires the same equipment as for the machining process by which the polymer surfaces are initially created. The surface coverage density of nanoparticles was manipulated by optimizing operating parameters. Finally, the resulting change in wettability caused by the changes in surface chemistry and roughness was measured by X-ray photoelectron spectroscopy (XPS) and dynamic contact angle measurements.

6.3 Material and methods

6.3.1 Materials

For PET, 4 by 4 mm square samples were cut from a 1.5 mm thick commercially available sheet (McMaster-Carr, USA). The sides were polished with 1200 grit silicon carbide paper in a grinder/polisher (Leco SS-200, USA) in order to improve baseline accuracy during advancing and receding contact angle measurements. Similarly, 1 by 1 cm square titanium samples were cut from a sheet with a thickness of 0.5 mm (McMaster-Carr, USA).

6.3.2 Laser system

Micromachining and PLD were performed using an amplified Ti:sapphire laser (Coherent Libra, USA) which emits a horizontally polarised Gaussian beam of 800 nm wavelength, 4 W output power, in pulses of 150 fs pulse duration, and at a repetition rate of 1 kHz. The beam power is controlled through a variable attenuator which consists of a half-wave plate and a polarising beam splitter. The beam is then focused using a 100 mm plano-convex lens down to a theoretical $1/e^2$ spot size of 44 µm onto a motorised 3D translational stage (Newport Corporation, USA) which is subjected to the stationary laser beam. The stage's movement and velocity were digitally controlled via the GOL3D software (GBC&S, France) along with a mechanical shutter (Uniblitz, USA).

6.3.3 Porous PET surface preparation

The porous, high surface area microstructures that served as substrates for PLD were created by femtosecond laser micromachining of the PET samples at focus. As outlined in our previous work [94], the machining procedure involves simple raster scanning of the laser beam on the sample surface at a single pulse peak fluence $F_0=3.9$ J/cm² with 55 pulses-per-spot (*PPS*). Figure 50 illustrates the resulting increase in surface roughness and porosity. Immediately after machining, all samples were placed in a sonication ethanol bath for five minutes to remove any loose machining debris.



Figure 50: Comparison between a) pristine and b) micromachined PET.

6.3.4 Atmospheric PLD setup

The pulsed laser deposition setup is illustrated in Figure 51. The titanium target and surface modified PET substrate were placed in parallel at an adjustable distance d^* from each other and at a 45° angle with respect to the incoming beam. Titanium ablation was performed by linearly translating the sample holder with respect to the stationary beam over a distance of 5 mm in order to cover all of the substrate. The ablated line was overscanned several times with the overscan number n and scanning velocity v used as adjustable operating parameters. Finally, for each sample, the whole process was repeated 4 times while rotating the substrate by 90° in between each run in order to ensure homogeneous nanoparticle deposition.



Figure 51: Schematic of PLD setup.

6.3.5 Surface analysis

Advancing (θ_A) and receding (θ_R) contact angles were measured at room temperature using a goniometer (DataPhysics OCA 15EC, USA). An initial droplet size of 2 µL of filtered reverse osmosis water (<10 ppb dissolved solids, 1-2 µS/cm conductivity) was used in the measurements. The droplet size was increased to 4 µL with a dispense rate of 0.1 µL/s and then reduced back to the original volume at the same rate. Three separate measurements were performed for each sample.

Chemical characterisation of the various films was performed via X-ray photoelectron spectroscopy (XPS) (ThermoFisher scientific K-alpha, USA). Measurements were taken using a 400 µm spot size with an Argon ion flood gun turned on in order to compensate for surface charging. Two types of scans were performed for each sample. A survey scan (200 eV pass energy, 3 scans, 10 ms dwell time) in order to determine composition and high resolution scans (50 eV pass energy, 10 scans, 50 ms dwell time) for the 1s sublevel of Carbon and Oxygen and the 2p sublevel of titanium in order to determine bonding structure.

The surface topography was imaged via scanning electron microscopy (SEM) (FEI Inspect F50, USA). This required coating the samples with a very thin (1-2 nm) layer of gold by low-vacuum sputtering in order to avoid surface charging.

6.4 Results and discussion

6.4.1 Effect of target-substrate distance

As a first step, PLD was performed at different distances d^* to determine how close target and substrate have to be to one another in order for particle plume impingement to occur. Figure 52 illustrates the resulting surface textures after PLD at a single pulse peak fluence $F_0=19.7$ J/cm², an overscan number n=16, and a scanning velocity v=0.3 mm/s which corresponds to a pulse-perspot number *PPS*=147.



Figure 52: Effect of target-substrate distance on nanoparticle deposition with F₀=19.7 J/cm², n=16, and v=0.3 mm/s.

At $d^{*=1}$ and 2 cm, which are distances that are in-line with classic low-pressure PLD operation, no nanoparticle coverage was observed. Nanoparticles only appeared at a target-substrate distance of 1 mm. The requirement of a much smaller d^{*} for atmospheric PLD can be explained by the plume dynamics during laser ablation. After a laser pulse is absorbed and ionisation of the target occurs, a plasma plume is formed that expands adiabatically until its pressure is equilibrated by that of the background gas [218]. The maximum plume length *L* can then be described by the adiabatic expansion model:

$$L = A[(\gamma_h - 1)E]^{\frac{1}{3\gamma_h}} P_{\infty}^{-\frac{1}{3\gamma_h}} V^{\frac{\gamma_h - 1}{3\gamma_h}}$$
(35)

$$A = \left(1 + \frac{1}{\tan\theta}\right) \left(\frac{3\tan\theta}{\pi + 2\pi\tan\theta}\right)^{\frac{1}{3}}$$
(36)

$$V = \nu \tau a \tag{37}$$

Where *E* is the laser pulse energy, P_{∞} is the background gas pressure, *V* is the plasma volume at the end of the laser pulse, *v* is the plasma expansion velocity, τ is the pulse duration, *a* is the beam spot area, γ_h is the specific heat ratio, and *A* is a geometrical factor that is dependent on the plume expansion angle θ . Values of *v* and θ were measured to be 4800 m/s and 35° respectively in a previous synchronised videography study of the expanding plume performed using our laser setup [219]. This results in a plasma length of *L*=0.2 mm. At this distance from the target, nanoparticles start to aggregate due to collisions with the background gas molecules and diffuse in the direction of the substrate. Amoruso et al. have shown that, in the case of fs ablation of metallic targets, the kinetic energy of the nanoparticles is still high enough that they are able to travel distances up to eight times farther than the plasma plume [220]. In our case, this corresponds to a distance of 1.6

mm. Therefore, by using fs laser pulses and a setup that allows us to place the substrate within the range of the nanoparticle plume, PLD was successful without the need for low-pressure conditions.

Furthermore, the shape of the nanoparticles that were deposited was of interest since they formed a web-like structure consisting of nanochain wires linked through agglomerate nodes. Sivakumar et al. have demonstrated the formation of the same type of nanoparticle web by ablating titanium [221]. Their transmission electron microscopy (TEM) analysis showed that these nanochains are formed by individual nanoparticles fused together by an oxide layer formed by reaction with air. The authors were only able to create such structures by operating in the MHz regime which they dubbed as the frequency threshold for nanoweb formation. However, our study shows that this type of nanoparticle structure can be achieved at 1 kHz. Their proposed hypothesis for the frequency dependence of the microstructure formation is that, during femtosecond laser ablation, nanoparticles are mostly formed through vapour condensation on a picosecond timescale while agglomerates form by particle collision in the expanding plume on a timescale of around 1 us. Therefore, when ablating in the MHz regime, a constant supply of nanoparticles can be generated on a timescale shorter than that of aggregate formation. This greatly increases the collision probability and allows the formation of agglomerates that are much more ordered than the random stacking typically observed in the Hz and kHz regime. In our case, due to the extremely small distance between target and substrate, there is a large degree of interaction between the yetexpanding plume and the flux of nanoparticles that have already reached the surface and are being sputtered back in the opposite direction. This greatly increases the collision probability inside the plume which explains why we observed nanochain formation at a much lower repetition rate.

6.4.2 Optimisation of scanning velocity and overscan number

The next step was to optimise the scanning velocity and overscan number in order to minimise the time required for PLD while still achieving an acceptable amount of nanoparticle incorporation. Figure 53 illustrates the resulting microstructures (F_0 =19.7 J/cm²).



Figure 53: Effect of overscan number and scanning velocity on nanoparticle deposition.

No nanoparticle coverage was observed for n=1, while the coverage was very limited for n=2 despite the high operating fluence. This indicates that very high ablation depths and therefore large quantities of material ablation are required for successful deposition which again is due to the high collision frequency required for nanoweb formation. As for the effect of scanning velocity, limited coverage was observed at v=0.6 mm/s. Interestingly, operating at a very low scanning speed (v=0.1 mm/s) decreased the nanoweb homogeneity with the network being characterised by larger, less interconnected agglomerates. This is somewhat counterintuitive as a lower scanning speed increases the *PPS* number and thus the ablation depth. One possibility is that the now very high flux of impinging nanoparticles starts sputtering the already deposited film thus causing the less agglomerated regions to break off. Following these results, n=16 and v=0.3 mm/s were chosen as operating parameters for the rest of the experiments.

6.4.3 Effect of nanoparticle coverage on wettability

After establishing the process parameters for successful fs PLD of titanium onto micromachined PET, we investigated the possibility of tuning wettability by controlling the density of deposited nanoparticles. Pristine PET has a mildly hydrophobic advancing contact angle (θ_A) of 92 ± 2^0 and a hydrophilic receding contact angle (θ_R) of 57 ± 2^0 . After micromachining, the porous PET surface structure is more hydrophilic than the pristine PET with a θ_A of 82 ± 2^0 and a θ_R of 43 ± 2^0 . This is in line with Wenzel theory since the increase in liquid-solid contact area induced by the large increase in roughness and porosity after machining enhances the intrinsic hydrophilicity of the material. There is also the possibility of a laser-induced increase in polar surface functional groups since photochemical reactions have been reported to occur on polymer surfaces during femtosecond laser micromachining [4]. However, our XPS analysis showed no significant difference in composition before and after machining as the atomic carbon-to-oxygen ratio was close to the stoichiometric value of 2.5:1. Figure 54 presents the nanoparticle coverage and the resulting contact angles as a function of PLD operating fluence.



Figure 54: Surface coverage and contact angles as a function of fluence. Error bars represent the standard deviation of three measurements. Contact angle values of 0° represent cases where wetting was so prominent that the full extent of the sample was covered by the water droplet. They do not represent actual measurements.

For fluences below $F_0=10 \text{ J/cm}^2$, nanochains are only deposited in between the substrate features which results in a partial coverage regime. ARCA measurements on these two samples demonstrated a significant increase in hydrophilicity in comparison with the micromachined sample. This decrease in measured contact angles correlates with increasing fluence. On the other

hand, for operation at fluences above $F_0=10$ J/cm², complete surface coverage by a heavily interconnected nanoweb was observed. This led to the water droplets completely wetting the sample surface and therefore rendering ARCA measurements impossible. This extremely hydrophilic behaviour is initially surprising as this very large degree of porosity and nanoroughness is usually expected to favour air trapping and therefore Cassie state wetting. Yet, the observed hydrophilicity can be explained by considering both the chemistry and topography of the deposited nanoweb. The SEMs show that the nanoweb structure exhibits features at different heights, as seen from the bright nodes which are located higher than the darker ones. Since the distance between these highest agglomerate nodes is varying and considerably larger than the average pore size, sagging of the water-air interface of a deposited droplet occurs. Thus, the sagged triple line gets in closer proximity to the lower located nodes which, due to the polar nature of the titanium oxide molecules, attract the sagging water interface to a degree that overcomes surface tension. The resulting increase in liquid-solid contact with the highly hydrophilic nanoparticles leads to complete wetting of the nanoweb. As a next step, all samples were subjected to vigorous sonication in an ethanol bath in order to assess the stability of nanoparticle incorporation into the substrates.

6.4.4 Stability of nanoparticle incorporation

Figure 55 presents the resulting microstructure after sonication. The SEM corresponding to $F_0=6.6 \text{ J/cm}^2$ clearly shows that the nanochains deposited in the partial coverage regime were not solidly attached to the surface as no nanoparticles remained after sonication. However, for fluences higher than $F_0=10 \text{ J/cm}^2$, an increasing amount of small spherical nanoparticle clusters was observed. This implies that the full coverage by the nanochain web observed before sonication constituted a weakly attached outer layer that was growing on top of the clusters that are actually strongly attached to the surface. Furthermore, the results shown in Figure 55 clearly demonstrate that nanoparticle coverage density can be controlled by operating fluence as the coverage observed ranged anywhere from light decoration of surface features ($F_0=13.2 \text{ J/cm}^2$), to full surface coating that follows the texture of the substrate ($F_0=19.3 \text{ J/cm}^2$), to the obstruction of the original pore structure by thick layer deposition ($F_0=32.9 \text{ J/cm}^2$). The fact that surface coverage is correlated to fluence is due to the fact that, at higher energies, the kinetic energy of the nanoparticle plume is much higher meaning that a larger portion of impinging particles will adsorb to the substrate.



Figure 55: Evolution of remaining nanoparticle coverage as a function of fluence after sonication in ethanol.

As shown in Figure 56, the decrease in contact angle correlates very well with the increase in nanoparticles firmly attached to the surface. Below $F_0=10$ J/cm², samples that observed nanochain incorporation and were significantly more hydrophilic than the original substrate before sonication now observed little change in wettability due to the removal of weakly adhered nanoparticles by sonication. Between $F_0=10$ J/cm² and $F_0=19.3$ J/cm², wettability variation is clearly achieved as the samples are increasingly hydrophilic with an almost linear decrease in advancing contact angle owing to the steady increase in nanoparticle coverage density. Finally, once titanium nanoparticles cover the entirety of the underlying microstructure, complete wetting is achieved again. In conclusion, these results demonstrate that any wetting behaviour between that of the original substrate surface and the fully wetted one can be easily achieved by finely controlling nanoparticle deposition through operating fluence adjustment.



Figure 56: Evolution of contact angles as a function of fluence. Error bars represent the standard deviation of three measurements. Contact angle values of 0° represent cases where wetting was so prominent that the full extent of the sample was covered by the water droplet. They do not represent actual measurements.

Finally, the evolution of surface chemistry with the increasing nanoparticle coverage was measured via XPS as presented in Figure 57. A clear increase in titanium content which correlates with the observed increase in nanoparticle coverage is observed. The accompanying increase in oxygen and sharp decrease in carbon suggests that titanium is indeed being deposited as an oxide. This was confirmed by the high-resolution spectra as illustrated in Figure 58. The spectrum of titanium clearly shows the presence of TiO_2 as it is composed of its $Ti2p_{3/2}$ (458.5 eV) and $Tip_{1/2}$ (464.5 eV) spin-orbital components as well as the typical satellite feature at 472 eV. This is further confirmed by the oxygen spectrum which is composed of a convoluted peak at 533 eV which represents the single and double carbon-oxygen bonds and a large peak at 530 eV which is typical of metallic oxides. From the peak areas, the ratio of oxygen-titanium to oxygen-carbon bonds was calculated to be 1.8. Knowing the composition of the sample and that of the original substrate, the fraction of oxygen that was not originally on the surface can be estimated to be 29 at% which suggests a stoichiometric oxidation of the nanoparticles which is typical for PLD operation in an oxygen environment [222].



Figure 57: Evolution of surface chemistry as a function of fluence.



Figure 58: High-resolution spectra of a) 2p sublevel of titanium and b) 1s sublevel of oxygen after PLD at F₀=16.4 J/cm².

Thus, by introducing controlled amounts of nanoparticles which are very hydrophilic in nature, we have created a composite surface with a controllable composition. Going back to Cassie-Baxter theory, this means that this novel technique achieves wettability variation by taking advantage of both the nanoroughness and the inherent wettability of the added nanoparticles without compromising the structure of the underlying porous substrate.

6.5 Conclusions

Through the successful and controllable incorporation of titanium nanoparticles into a porous PET microstructure by pulsed laser deposition, successful variation of wettability was achieved while preserving the substrate topography. The use of a femtosecond laser source, coupled with the use of a 1 mm target-substrate distance, allowed the successful impingement of the nanoparticle plume on the substrate at atmospheric conditions. The traditional need of PLD to operate in vacuum was therefore circumvented. Increased collision probability in the plume due to recoil from the substrate led to the formation of an extremely hydrophilic titanium dioxide nanoweb. Sonication in an ethanol bath led to the detachment of the nanoweb revealing nanoparticle clusters that were strongly attached to the substrate. The inclusion of these clusters created a composite surface with controllable composition. Due to the inherent nanoroughness and chemical hydrophilicity of this added component, successful wettability variation was achieved. This work therefore highlights atmospheric pulsed laser deposition using a femtosecond laser as a simple and vacuum-free process for the modification of the wetting properties of hierarchical and high surface area polymers without compromising their topology. The practicality of this technique is further compounded by the fact that it requires the same equipment as the machining process with which the substrates are initially prepared.

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Conflicts of Interest

The authors declare no conflicts of interest.

Chapter 7 Conclusions

7.1 Summary

Within the framework of this thesis, a detailed investigation of femtosecond laser micromachining of polymer surfaces was performed. Through this study, the mechanisms behind the formation of hierarchical porous surfaces were identified and verified through crystallographic measurements. A comprehensive characterization of the optical and chemical properties of these structures was also performed. Furthermore, the viscoelastic properties that control pore dimension were identified. Finally, a novel pulsed laser deposition setup for the wettability tuning of laser-induced porous surfaces was developed.

An initial parametric study on six different materials indicated that porous network structures can form on a wide variety of polymers. Operation slightly above threshold fluence and at low pulse numbers was observed to promote porous structure formation. Indeed, for polymers with a very low threshold fluence, ablation was observed to dominate over porous structure formation. A similar observation was made by comparing the machining behavior at two separate wavelengths (λ =275 nm and λ =800 nm). Porous structure formation was severely inhibited during UV irradiation due to the increased absorption leading to lower threshold fluences. Wavelength was also observed to have a significant effect on incubation. Indeed, when operating above the cutoff wavelength, a transition from multiphoton absorption at low pulse numbers to linear absorption at high pulse number occurs which leads to significant incubation. This phenomenon was observed to be more prevalent for polymers that are susceptible to photo-oxidation. These observations are all consistent with an explosive boiling mechanism. In this hypothesis, for polymers with a low threshold fluence, the surface melt layer does not get heated past the critical temperature for homogeneous bubble nucleation since most of the incoming energy is directly converted into material ionization.

Evidence of explosive boiling was later put forth through grazing incidence x-ray diffractometry. The crystallinity and crystal structure of both machined and pristine high-density poly(ethylene) were investigated. Results showed that femtosecond laser machining led to a local

decrease in crystallinity and the formation of a new monoclinic phase that is typically only formed at high temperatures and pressures. After annealing, the original crystal structure was recovered and the crystallinity increased. Thus, laser induced porous structures consist of a rapidly quenched melt layer and the pores correspond to the remnants of the volume occupied by gas bubbles during phase explosion. Since bubble growth in a melt depends on its viscoelastic properties, poly(ethylene) grades with increasing molecular weights were machined and rheologically characterized. Apart from very low molecular weights, increasing molecular weight was observed to decrease final pore size. This is due to the increase in viscosity which in turn decreases bubble growth rate during explosive boiling.

Finally, atmospheric pulsed laser deposition was highlighted as a novel technique for the wettability tuning of femtosecond laser-induced porous structures. The combination of femtosecond pulses with a millimetric target-substrate distance allowed the successful incorporation of titanium nanoparticle clusters into porous poly(ethylene terephthalate). The inclusion of these nanometric hydrophilic heterogeneities created a composite surface with two components. The extent of surface nanoparticle coverage was controlled by the operating fluence. As a consequence, successful wettability modification was achieved. The practicality of this technique lies in the fact that it requires the same equipment as for laser machining and does not require a vacuum environment.

7.2 Recommendations for future work

The research presented in this work sets the groundwork for the future optimization and implementation of femtosecond laser-induced porous polymer structures in industrial applications. Highlighted below are several research avenues that require further investigation and can be expanded upon.

• While the mechanism behind laser-induced porous structure formation has been identified, several aspects of laser-induced structure formation remained unexplained. For example, it is unclear whether the structure bundling and deterioration observed in Chapter 3 are due to hydrodynamic effects, nanoparticle redeposition, or a combination of both. Furthermore, in Chapter 4, novel microstructures with unknown formation mechanism were observed to appear upon UV irradiation such as the circular holes on LDPE and periodic structures on PET. Thus, significant research

space is left unexplored in the field of polymer response to fs laser irradiation.

- In Chapter 4, the transition from a multiphoton absorption process at low pulse numbers to linear absorption at high pulse numbers was observed to significantly contribute to incubation effects. While this observation helps qualitatively identify the non-linear optical processes at hand, the quantitative relationship between the two phenomena remains unclear. Thus, the development of an extension of the incubation model that explicitly includes the optical properties of transparent materials is still lacking.
- In Chapter 5, the role of the viscoelastic melt properties on pore size was highlighted. However, this was only demonstrated on a single pure polymer. Thus, the full extent of achievable pore dimensions is still unclear. One research avenue which is relevant for industrial applications would be to explore the effect of plasticizers which decrease polymer melt viscosity.
- The pulsed laser deposition setup presented in Chapter 6 has some room for improvement. The modularity of the setup could be improved to accommodate samples of all sizes and thicknesses. Furthermore, the stage supporting the substrate could be modified so as to be allowed to rotate. This would minimize operator handling and improve homogeneous nanoparticle distribution on the surface. Finally, several combinations of hydrophilic/hydrophobic targets and substrates can be tested to assess the full range of achievable wettabilities.
- Finally, the new insight into femtosecond laser-induced porous structure formation highlighted in this thesis can be applied for the design and optimization of novel engineering materials. For example, pore dimensions can be optimized on biocompatible polymers in order to target specific cells and enhance their attachment and growth on the surface. Relevant examples include enhanced endothelialization on synthetic grafts and stents and enhanced tissue formation on biodegradable scaffolds.

7.3 Original Contributions

The original contributions to knowledge presented in this thesis are summarized below:

1. Production of novel porous microstructures with hierarchical roughness on a wide

variety of polymers and identification of the favorable operating conditions and material-dependent parameters for their formation.

- 2. Optical and chemical characterization of femtosecond laser-induced structures on a variety of polymer surfaces at two separate wavelengths.
- 3. Determination of the relationship between the optical and chemical properties and incubation effects.
- 4. Identification of explosive boiling as the formation mechanism behind femtosecond laser-induced porous structures. Presentation of crystallographic evidence supporting the fact that such structures result from a quenched melt layer undergoing phase explosion.
- 5. Determination of the macromolecular and viscoelastic melt properties that dictate final pore size.
- 6. Development of a novel pulsed laser deposition setup for the wettability modification of laser-induced structures that does not compromise the porous topology.
Appendix A



Figure A1: Lacunarity curves at different fluences for HDPE at PPS=55.



Figure A2: Lacunarity curves at different fluences for PC at PPS=55.



Figure A3: Lacunarity curves at different fluences for PLA at PPS=55.



Figure A4: Lacunarity curves at different fluences for PMMA at PPS=55.



Figure A5: Lacunarity curves at different fluences for PTFE at PPS=55.



Figure A6: Modified depth as a function of fluence for HDPE patches at PPS=55.



Figure A7: Modified depth as a function of fluence for PET patches at PPS=55.



Figure A8: Modified depth as a function of fluence for PLA patches at PPS=55.



Figure A9: Modified depth as a function of fluence for PMMA patches at PPS=55.



Figure A10: Modified depth as a function of fluence for PTFE patches at PPS=55.



Figure A11: Line width results for HDPE. The error bars represent the standard deviation of three measurements. The dashed lines represent the best fit of equation 23.



Figure A12: Line width results for PC. The error bars represent the standard deviation of three measurements. The dashed lines represent the best fit of equation 23.



Figure A13: Line width results for PET. The error bars represent the standard deviation of three measurements. The dashed lines represent the best fit of equation 23.



Figure A14: Line width results for PMMA. The error bars represent the standard deviation of three measurements. The dashed lines represent the best fit of equation 23.



Figure A15: Line width results for PTFE. The error bars represent the standard deviation of three measurements. The dashed lines represent the best fit of equation 23.

Appendix B



Figure B1: Evolution of the transmittance spectrum of LDPE as a function of fluence for patches machined at PPS=55.



Figure B2: Evolution of the transmittance spectrum of PET as a function of fluence for patches machined at PPS=55.



Figure B3: Evolution of the transmittance spectrum of PLA as a function of fluence for patches machined at PPS=55.



Figure B4: Evolution of the transmittance spectrum of PMMA as a function of fluence for patches machined at PPS=55.



Figure B5: Evolution of the transmittance spectrum of PTFE as a function of fluence for patches machined at PPS=55.



Figure B6: Ablation depth per pulse for LDPE at λ =800 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and four-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B7: Ablation depth per pulse for PC at λ =800 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B8: Ablation depth per pulse for PET at λ =800 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B9: Ablation depth per pulse for PMMA at λ =800 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B10: Ablation depth per pulse for PTFE at λ =800 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B11: Ablation depth per pulse for LDPE at λ =275 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and two-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B12: Ablation depth per pulse for PC at λ =275 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B13: Ablation depth per pulse for PET at λ =275 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B14: Ablation depth per pulse for PLA at λ =275 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and two-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B15: Ablation depth per pulse for PMMA at λ =275 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.



Figure B16: Ablation depth per pulse for PTFE at λ =275 nm for a) multi-pulse ablation and b) single-pulse ablation with a comparison between the best fits of the linear and three-photon absorption models. Error bars represent the standard deviation of three measurements.

Appendix C



Figure C1: Viscoelastic properties versus angular frequency for Grade 1 at 190°C.



Figure C2: Viscoelastic properties versus angular frequency for Grade 2 at 190°C.



Figure C3: Viscoelastic properties versus angular frequency for Grade 3 at 190°C.



Figure C4: Viscoelastic properties versus angular frequency for Grade 4 at 190°C.



Figure C5: Viscoelastic properties versus angular frequency for Grade 5 at 190°C.



Figure C6: Viscoelastic properties versus angular frequency for Grade 6 at 190°C.

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