Femtosecond laser interaction with polystyrene and its wettability characteristics

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**FEMTOSECOND LASER INTERACTION WITH
POLYSTYRENE AND ITS WETTABILITY
CHARACTERISTICS**

WANG BING

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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**FEMTOSECOND LASER INTERACTION WITH
POLYSTYRENE AND ITS WETTABILITY
CHARACTERISTICS**

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partial fulfilment of the requirement for the degree of Doctor of
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Abstract

Ultrashort pulsed laser polymer processing has attracted much interest recently. Ultrashort pulsed laser has an advantage in the processing of transparent and dielectric materials due to its high intensity and short pulse duration. Many investigations have been conducted in this area. However, there are still important issues yet to be clarified and resolved. These include a rigorous and quantitative investigation on the nonlinear absorption of laser power by the irradiated substrate, the associated thermal effects and heat conduction on the transparent materials (e.g. a transparent polymer). In addition, it is known that a short pulsed laser could modify the surface wettability of a polymer, but the linkage of the modification to nonlinear absorption has never been correlated.

Polystyrene (PS) is a versatile polymer with many applications; many of these applications can take advantage of the different wettability if available. As PS is transparent to the wavelength of femtosecond laser employed for this investigation, PS is a natural choice for the current investigation.

In the current study, the nonlinear absorption behavior of thick transparent PS samples were theoretically analyzed and experimentally investigated by applying the z scan technique. The thick PS sample was treated as a stack of thin samples and the nonlinear absorption behavior at different laser powers were investigated. The nonlinear absorption coefficient of PS was quantified to be 0.000695 m/W.

The absorbed laser energy by the PS substrate will subsequently be converted to heat energy, and be conducted away. This femtosecond laser induced thermal effects

during the laser-polymer interaction process have been investigated experimentally and by simulation. Experimentally, the temperature changes at different sample z positions associated with different laser intensities were directly measured using an infrared camera calibrated for temperature measurements. For the same incident laser power, it was observed that the temperature increased more when the sample was placed near to the focal position. This was due to the higher laser intensity at the focal position, resulted in higher laser power absorption and thus higher sample temperature.

A 3D FE model based on the observed nonlinear absorption was constructed to simulate the heat conduction within the substrate at different z positions. The simulated results were compared with the experimental results. Good agreements were obtained between the simulated and experimental results at $z = 2$ mm (with ablation) and $z = 4$ mm (without ablation) with less than 2% difference between them. At $z = 0$ mm (with ablation), the simulated temperature was higher than the experimentally measured results, with a difference as high as 21.5%. This was due to laser-induced ablation with plasma formation at the surface at this high laser intensity. A simple estimate shows that only a small amount of energy was used for material vaporization during ablation. Instead, plasma generation during ablation was deduced to consume a significant amount of energy, but still much less than the energy absorbed by the substrate. Indeed, heat conduction as a result of the absorbed laser power was significant and dominant, with or without ablation.

In addition to the investigation of laser-material interaction mechanism, the femtosecond laser-induced surface wettability modification of PS has also been studied. The surface water contact angle at different z positions (thus laser

intensities) and absorptions were studied. The results show that at high laser intensity, the laser power absorption was high; the surface became very rough and hydrophobic. At low laser intensity, the surface became relatively much smoother and hydrophilic.

For a rigorous investigation, different surface structures were created on the surface to modify the surface to either highly hydrophilic or superhydrophobic. The results show that with micro-scale grooves created on the sample surface, the surface became very rough resulting in hydrophobic and even superhydrophobic (WCA = 156.2°) surfaces. Under these conditions, surface structure was the main factor that determines the surface wettability, and was consistent with the Cassie-Baxter's model. The surface wettability of hydrophobic surfaces was examined to be stable over time after laser treatment as the surface structure remained the same over time.

With properly spaced micro-pits created on the surface, the PS sample became more hydrophilic. The surface wettability increased with the depth, size and density of the micro-pits. This was consistent with Wenzel's model. Since the pit depth was shallow, the substrate maintains high transparency after the laser treatment. After laser treatment, WCA recovery was found on hydrophilic surfaces, especially on highly hydrophilic surfaces. This was due to the decreased polar groups over time.

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1. Wang B, Wang XC, Zheng HY, Lam YC, Femtosecond laser-induced surface wettability modification of polystyrene surface, SCIENCE CHINA: PHYSICS, MECHANICS AND ASTRONOMY, 59(12), 124211, 2016.
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List of symbols

E_p	Photon energy (J)
E_g	Material bandgap (J)
h	Planck constant (Js)
$I_{(z)}$	Laser intensity at depth z (W/m ²)
α	Absorption coefficient (m ⁻¹)
I_o	Incident intensity (W/m ²)
m	Number of photons
I	Laser intensity (W/m ²)
ω	Laser frequency (Hz)
m_e	Electron mass (kg)
ϵ_0	Free space permittivity (F/m)
e	Charge of electron (C)
c	Light speed (m/s)
n	Linear refractive index
w	Beam radius (m)
F_0	Peak laser fluence (J/m ²)
F_{th}	Ablation threshold fluence (J/m ²)
α_{eff}	Effective absorption coefficient (m ⁻¹)
E_0	Laser pulse energy (J)
N	Number of pulses
δ_{them}	Thermal penetration depth (m)
k	Thermal conductivity (W/mK)
γ_{sa}	Solid-air interfacial tensions (dyn/cm)
γ_{sl}	Solid-liquid interfacial tensions (dyn/cm)

γ_{LA}	Liquid-air interfacial tensions (dyn/cm)
θ	Contact angle (°)
T	Absolute temperature (K)
TR	Normalized transmittance
k_B	Boltzmann constant (m^2kg/s^2K)
λ	Wavelength (nm)
σ	Stefan's constant (W/m^2K^4)
ε	Emissivity
z	Distance from the focal plane (mm)
z_0	Rayleigh range (mm)
β	Nonlinear absorption coefficient (m/W)
P	Laser power (W)
$P(z,t)$	Instantaneous transmitted power (W)
$P_i(t)$	Instantaneous incident power (W)
ρ	Material density (kg/m^3)
C_p	Specific heat capacity (J/kgK)
I_{in}	Incident laser intensity (W/m^2)
I_{in_p}	Peak incident laser intensity (W/m^2)
$I_{out\_i\_p}$	Transmitted peak laser intensity from layer i (W/m^2)
T_{amb}	Ambient temperature (K)
Ra_L	Rayleigh dimensionless numbers
Pr	Prandtl dimensionless numbers
Gr_L	Grashof dimensionless number

Chapter 1 Introduction

1.1 Background

Laser is an acronym for “light amplification by stimulated emission of radiation” [1]. Laser is widely used in industries, medicines and life science [2]. Its applications in industries include laser cutting, laser marking, laser welding, laser drilling, photolithography, laser peening, and laser heat treatment [1]. Laser is able to process a wide range of materials, including glasses, metals and polymers. It has advantages over conventional machining techniques (e.g., drilling, milling, and turning), which include speed of processing, reduced heat-affected zone and no tool wear due to its non-contact nature [3].

A laser can be classified into either continuous wave (CW) laser or pulsed laser according to its operation mode [4]. Ultrashort pulsed laser is generally defined as a pulsed laser with a pulse duration less than one picosecond [3]. The generation of ultrashort pulsed laser provides new possibilities for material processing [5-9], particularly in material micro-fabrications due to its precise ablation and modification capability [10]. Comparing with long pulsed laser, ultrashort pulsed laser produces smaller heat-affected zone (HAZ). Ultrashort pulsed laser-induced cutting, drilling, welding and surface treatments have gained a lot of interests in recent years. It has the advantages to process not only transparent, but also dielectric materials, such as glasses and polymers [11]. This is attributed to its short pulse duration and high power intensity.

Polymer is one of the most used materials beside metals, glasses and ceramics. It can take the form of fibers, plastics, cellulose, rubbers etc [12]. It has a broad range of properties and widely used in industries, chemistries, biotechnologies and life sciences. Recently, there are increasing research works on ultrashort pulsed laser processing of polymers due to its various applications [5-7, 9, 13].

1.2 Motivation

Photon absorption is the first step of laser-material interaction. Nonlinear absorption was induced during ultrashort pulsed laser-material interaction due to its short pulse duration and high laser intensity. Nonlinear absorption is especially important for materials which are transparent to the laser wavelength as nonlinear absorption has to be the dominant mechanism for any significant laser-material interaction. Z scan technique is a simple and efficiency technique that can be applied to study the nonlinear behavior of materials [14-26]. However, most investigations only focused on thin samples [27-29]. In practice, thick samples are more widely used. Thus, this investigation will be on the nonlinear behavior of thick polymer sample.

Thermal effects induced in materials are key factors to be considered during laser material processing. Thermal effects determine the heat conduction, heat affected zone (HAZ) and thus the precision, ablation depth and subsurface properties during surface treatment. A popular belief is that there are no or negligible thermal effects during ultrashort pulsed laser material processing [30, 31]. This belief is based on the reasoning that the pulse duration of an ultrashort pulsed laser is too short for any significant transfer of laser energy to the substrate material. However, recently thermal effects have been proven to be significant, such as laser-induced phase

transformation of metals [32, 33], thermal effects on dielectrics [34], semiconductors [35] and metals [36, 37] processed with ultrashort pulsed laser. The current studies are limited to 1D and 2D. The relationship between nonlinear absorption and heat conduction is yet to be systematically studied. Hitherto, a good understanding is lacking on the thermal effects of ultrashort pulsed laser processing of materials transparent to the laser wavelength, and in particular polymers.

Controlled modification of polymer surface wettability, to either hydrophilic or hydrophobic, is highly desirable for various applications [5, 6, 38, 39]. For example, super-hydrophobic surfaces will facilitate self-cleaning of contaminants. Surface wettability also determines the reagent flow behavior in microfluidic channels, and ease of adhesion of cells. In addition, highly hydrophilic surface can improve surface adhesion and wettability, with potential for coating and joining applications. Laser irradiation has been applied for surface modification of metals, polymers and semiconductors [7, 9, 39-43]. Ultrashort pulsed laser is increasingly used as a tool for surface treatment. In contrast to long pulsed laser, ultrashort pulsed laser can induce nonlinear absorption of photons and has much less thermal effects. In addition, the use of ultrashort femtosecond laser pulses allows treatment of features with micrometric precision, as the laser beam can be accurately positioned and tightly focused into a spot size of several microns. However, the mechanisms of ultrashort pulsed laser induced surface modification of polymer materials are yet to be fully understood. Polystyrene is a widely used thermoplastic polymer in microfluidic and biological devices. Hitherto, there is only limited investigation on laser-induced surface modification of polystyrene [44, 45].

The aim of this investigation is to develop a methodology with validation the quantification of nonlinear absorption for laser-material interaction. To avoid or minimize the complication of linear absorption, a transparent material, namely polystyrene, for the wavelength of the femtosecond laser, can be employed. Validation can be achieved by correlating the thermal field with the absorbed laser energy. In addition, the surface wettability modification of polystyrene with femtosecond laser should be investigated as hitherto there is no such investigation. This has practical value as polystyrene is a widely used polymer for various applications, and wettability is an important parameter for many of these applications.

1.3 Objectives

The objectives of this investigation are:

- 1 To study the femtosecond laser-induced nonlinear absorption behavior on a transparent polymer, namely polystyrene, and to determine its nonlinear absorption coefficient.
- 2 To investigate the thermal effects induced during femtosecond laser polystyrene processing and to correlate these effects with temperature changes during the processing.
- 3 To achieve controlled surface wettability modification (hydrophilic and hydrophobic) of polystyrene by ultrashort pulsed laser and to investigate the associated processing and sample surface parameters.

1.4 Scopes

The scopes of the investigations are:

1. To determine the nonlinear absorption coefficient of thick polystyrene by applying the z scan technique.
2. To investigate the temperature profile and heat conduction during ultrashort pulsed laser polystyrene processing with an infrared camera.
3. To simulate heat conduction during laser-polystyrene processing with the measured nonlinear absorption coefficient.
4. To compare the simulated results with measured experimental results.
5. To create controlled surface structure on polystyrene surface by laser irradiations for the investigation of surface wettability modification, which includes the effect of surface structure and surface chemistry on surface wettability.

1.5 Organization of the thesis

- The overall framework is introduced in chapter 1. In chapter 2, the fundamental concepts of laser-material interaction are introduced. Previous works on ultrashort pulsed laser induced nonlinear absorption are reviewed. Investigations on ultrashort pulsed laser-induced thermal effects are summarized. Basic concepts on wettability are introduced and previous work on laser-induced surface wettability modification is reviewed, with limitations discussed.
- In chapter 3, the research methodology is introduced. In this investigation, temperature during laser polymer processing is directly measured with an infrared camera, which is calibrated with thermocouples for this investigation.

- Photon absorption is an important phenomenon as it is the first step of laser-material interaction. Nonlinear absorption is induced and dominant the absorption process during femtosecond laser-material interaction especially for materials which are transparent to the laser wavelength. In chapter 4, the femtosecond laser-induced nonlinear absorption on polymer is discussed. The nonlinear absorption coefficient is determined by applying the z scan technique.
- Subsequent to energy absorption, the energy is dissipated into the bulk material as heat. Heat conduction and thermal effects are important as they have effects on the machining precision and material property after laser treatment. The thermal effect of ultrashort pulsed laser is significantly less as compared to long pulsed laser and continuous laser. However, as demonstrated by previous works (as discussed in chapter 2), there is still a large percentage of laser energy being converted to heat energy. Thus, in chapter 5, the femtosecond laser-induced thermal effects are investigated.
- In chapter 6, heat conduction as a result of laser-material interaction is simulated, with the obtained temperature fields compared with experiment results.
- In chapter 7, the application of laser polymer processing is discussed. Laser-induced surface wettability modification of PS is investigated. With simple laser treatment method, the PS surface can be tuned to either hydrophilic or hydrophobic. The relevant parameters on surface modifications are discussed.
- Chapter 8 presents the conclusions reached for this investigation, with future works suggested.

Chapter 2 Literature review

2.1 Introduction

Laser material processing is an important process and has various applications. Ultrashort pulsed laser-material interaction is a complex and nonlinear process. The interaction mechanism is different and much more complicated compared with long pulsed and continuous wave lasers. In this chapter, both long and ultrashort pulsed laser-material interaction mechanisms will be introduced. The laser-induced linear and nonlinear photon absorption, ablation and penetration depth are presented.

Photon absorption is an important phenomenon as it is the first step of laser-material interaction. Subsequent to energy absorption, the energy is dissipated into the bulk material as heat. Heat conduction and thermal effects are important as they have effects on the machining precision and material property after laser treatment. Previous works on the absorption coefficient determination and the ultrashort pulsed laser induced thermal effects are reviewed with their limitations discussed. In addition, previous works on laser-induced surface wettability modification are reviewed, together with the basic concepts on wettability.

2.2 Laser-material interaction mechanism

2.2.1 Photon absorption

2.2.1.1 Linear absorption

The first step of laser-material interaction is photon absorption. Photon absorption can be classified into linear and nonlinear absorptions. For linear absorption, the energy absorption increased linearly with the laser intensity (governed by Beer-

Lambert law) [46], while for nonlinear absorption the energy absorption increased nonlinearly with the laser intensity (e.g. second order absorption) [47, 48]. For continuous wave laser and long pulsed lasers, their energy intensity is not high enough to cause nonlinear absorption. Photon is absorbed through linear absorption. For ultrashort pulsed laser, nonlinear multiphoton absorption occurs due to the high laser intensity, which causes direct ionization. The nonlinear multiphoton absorption will be further discussed in section 2.2.1.2. For linear photon absorption, photon is absorbed only when its energy is larger than or equals to the material's bandgap [46].

$$E_p = h\nu \geq E_g \quad (2.1)$$

Where E_p is the photon energy, E_g the bandgap, h the Planck constant ($6.62606957 \times 10^{-34}$ Js), ν the frequency.

Linear absorption can be described by Beer-Lambert Law.

$$I(z) = I_o e^{-\alpha z} \quad (2.2)$$

where $I(z)$ is the laser intensity at depth z , α the absorption coefficient and I_o the incident intensity.

The absorption depth (penetration depth) is the depth whereby the laser intensity drops to $1/e$ of the initial incident intensity. It can be calculated as

$$d = \frac{1}{\alpha} \quad (2.3)$$

2.2.1.2 Ionization

For ultrashort pulsed laser, the intensity is sufficiently high to cause full ionization of almost any materials [48]. When polymers and dielectrics interact with a ultrashort pulsed laser with its wavelength in visible or near infrared spectra, the photon energy is less than the bandgap and thus the absorption is dominated by nonlinear absorption [47, 48]. For a nonlinear absorption dominant process, the ablation threshold highly depends on the bandgap since the bandgap determines the multiphoton absorption order [47]. There are two types of ionization, namely collisional impact ionization (avalanche ionization) and photoionization (multiphoton ionization and tunneling ionization) [47].

Collisional impact ionization

To activate avalanche ionization there must be sufficient free (seed) electrons in the conduction band. Photons are absorbed by free electrons via inverse bremsstrahlung process. When the kinetic energy of the free electrons is high enough (exceed the ionization bandgap), the energy can be transferred to the bound electrons by collision. As such, more free electrons are produced as depicted in Fig.2.1. Consequently, as the process is repeated, more and more free electrons are produced from the bound electrons. This process is called avalanche ionization, which is highly dependent on the free electron density [48]. When the laser intensity is below 10^{12} W/cm², avalanche ionization is responsible for initiating the ionization. With higher laser intensity, multiphoton ionization and tunneling ionization are responsible for initiating the ionization. When sufficient free electrons is generated, there are enough seed for avalanche ionization again [48].

Fig. 2.1 Collisional impact ionization [48].

Photoionization

At very high laser intensities (typically $> 10^{13} \text{ W/cm}^2$), an electron can absorb multiple photons to overcome the bandgap. This requires

$$m h \nu \geq E_g \quad (2.4)$$

where m is the number of photons. Multiphoton absorption is through direct ionization as shown in Fig.2.2. By going through several metastable quantum states, the absorption process can be achieved. It is an m^{th} order process. At low laser intensity, the multiphoton absorption cross section is small, and thus the laser intensity should be increased to achieve significant multiphoton absorption [48]. However when the laser intensity exceeds a threshold limit (typically $> 10^{15} \text{ W/cm}^2$), tunneling ionization effect occurs.

Fig. 2.2 Multiphoton ionization [48].

Under very high laser intensity (typically $> 10^{15} \text{W/cm}^2$), the band structure is distorted. The barrier between the valence and conduction bands is reduced. Electron can directly proceed to the conduction band from the valence band by quantum tunneling [47]. The transition of multiphoton ionization to tunneling ionization is governed by Keldysh parameter:

$$\gamma = \frac{\omega}{e} \sqrt{\frac{m_e c n \epsilon_0 E_g}{I}} \quad (2.5)$$

where I is the laser intensity, ω the laser frequency, m_e the electron mass, ϵ_0 the free space permittivity, e the charge of electron, c the light speed and n the linear refractive index. For $\gamma < 1.5$, the process is dominated by tunneling ionization; for $\gamma = 1.5$, the process is dominated by both multiphoton ionization and tunneling ionization; for $\gamma > 1.5$, the process is dominated by multiphoton ionization, see Fig.2.3 [49].

Fig. 2.3 Photoionization under different Keldysh parameters [49].

At high laser intensity, free electrons can be produced through multiphoton and tunneling ionizations. These free electrons become the seed for avalanche ionization.

Thus at high laser intensity, avalanche ionization also occurs after multiphoton ionization and/or tunneling ionization as depicted in Fig.2.4 [47].

Fig. 2.4 Photoionization followed by impact ionization: a) multiphoton ionization, b) tunneling ionization and c) avalanche ionization [47].

2.2.2 Ablation

Free electron buildup is a necessary step to initiate laser ablation [48]. Ablation occurs when the laser fluence exceeds the ablation threshold. Subsequently plasma is formed and confined to the surface. Laser-plasma interaction causes further damage of the bulk material [3]. For a Gaussian beam, the laser intensity distribution can be expressed as:

$$I_{(r)} = I_0 e^{\frac{-2r^2}{w^2}} \quad (2.6)$$

where I_0 is the center beam intensity at radius $r = 0$, w is the beam radius [4]. The fluence distribution of a Gaussian beam is presented in Fig.2.5.

Fig. 2.5 Gaussian beam profile [11].

As depicted in Fig. 2.5, F_0 is the peak fluence, F_{th} represents the ablation threshold fluence, and w_0 is the beam radius at the distance where laser fluence drops to $1/e^2$ of its original values.

The laser ablation depth per pulse can be calculated as [11]:

$$d = \frac{1}{\alpha_{eff}} \ln\left(\frac{F_0}{F_{th}}\right) \quad (2.7)$$

where α_{eff} is the effective absorption coefficient. Ultrashort pulsed laser experiments have reported that α_{eff} is almost equals to α (linear absorption coefficient) for samples with strong absorption e.g. metals. However, for samples with weaker absorption, e.g. dielectrics, α_{eff} is larger than α [11]. Evaluation of ablation threshold F_{th} by employing Eq.2.7 is difficult. The measurement of ablation depth especially for cavity is difficult. In particular, α_{eff} is difficult to estimate for a nonlinear absorption process. One solution to this difficulty is a self-consistent evaluation of ablation threshold and beam diameter as shown in Fig 2.6.

Fig. 2.6. Laser ablation of sample (top) and corresponding fluence distribution (bottom) [11].

The relation between ablation diameter and threshold fluence can be expressed as [11]:

$$D^2 = 2w_0^2 \ln\left(\frac{F_0}{F_{th}}\right) \quad (2.8)$$

$$F_0 = \frac{2E_0}{\pi w_0^2} \quad (2.9)$$

Where E_0 is the pulse energy, F_0 the peak fluence (at the center of the laser beam), F_{th} the ablation threshold. Eq. 2.8 may be re-written in terms of pulse energies [11]:

$$D^2 = 2w_0^2 \ln\left(\frac{E_0}{E_{th}}\right) \quad (2.10)$$

where E_{th} is the energy ablation threshold. By plotting D^2 vs E_0 in a semi-logarithmic plot, the beam radius w_0 can be obtained from the slope. With known beam radius and equation 2.9, a semi-logarithmic plot of D^2 vs F_0 can be obtained which will allow the deduction of the ablation threshold F_{th} , see for example Fig.2.7.

Fig. 2.7 Polyimide treated with femtosecond laser ($\tau=150\text{fs}$, $\lambda=800\text{nm}$, circularly polarized light). Squared diameter vs laser fluence under different pulses. Solid line: focusing with $f = 25\text{ mm}$ lens, dash line focusing with $f = 60\text{ mm}$ lens [11].

Fig. 2.7 indicates that as the number of pulses increases, the laser ablation threshold decreases. This is due to the incubation effect, which can be expressed as [11]:

$$F_{th}(N) = F_{th}(1)N^{\xi-1} \quad (2.11)$$

where N is the number of pulses, $F_{th}(N)$ the laser ablation threshold at N number of pulses, and $F_{th}(1)$ the ablation threshold of a single pulse. The incubation parameter ξ indicates the degree of incubation effect. When $\xi = 1$, there is no incubation effect. Table 2.1 shows some examples of incubation effect of ultrashort pulsed laser interacting with polymers [11].

Table 2.1 Laser ablation threshold $F_{th}(N)$ and incubation parameter ξ . ($\tau=150\text{fs}$, $\lambda=800\text{nm}$) [11]

	$F_{th}(N)$ [Jcm^{-2}]				ξ
	$N=1$	$N=5$	$N=10$	$N=100$	
PI	1.0	0.8	0.7	0.5	0.9
c-PET	1.8	1.5	1.0	0.3	0.6
a-PET	2.1	1.5	1.0	0.4	0.6
PC	1.8	1.4	1.2	0.5	0.7
PTFE	1.9	1.4	1.2	0.7	0.8
PMMA	2.6	2.3	1.5	0.6	

2.2.3 Penetration depth

Penetration depth includes optical penetration depth and thermal penetration depth. Generally, in the context of laser-material interaction, penetration depth refers to optical penetration depth [50, 51]. It measures how deep light or any electromagnetic radiation can penetrate into the materials. It is defined as the depth at which the intensity of radiation inside the material falls to $1/e$ (around 37%) of its original value at (or more precisely, just beneath) the surface. For an electric or electromagnetic field to reduce to $1/e$, its power reduces to $1/e^2$. The length for power to drop to $1/e^2$ equals to the skin length (skin depth/skin layer) [52]. When electromagnetic radiation is incident on the surface of a material, it may be partially reflected from that surface and there will be a field containing energy transmitted into the material. This electromagnetic field interacts with the atoms and electrons inside the material. Depending on the nature of the material, the electromagnetic field might travel far into the material, or may die out very quickly. For a given material, the penetration will generally be a function of wavelength. For a continuous laser and a long pulsed laser, the optical penetration depth can be

calculated by applying equation 2.3. For ultrashort pulsed lasers, the calculation is more complex due to their nonlinear absorption.

Thermal penetration depth generally refers to the thermal or heat diffusion length. After absorption, the absorbed energy is diffused into the material. The diffuse distance is the thermal diffusion length. Thus, it determines the HAZ. Sometimes thermal penetration depth is also defined as a combination of optical penetration depth and thermal diffusion length [53]. The thermal diffusion length is given as

$$\delta_{them} = \sqrt{at_i} \quad (2.12)$$

$$a = \frac{k}{\rho c} \quad (2.13)$$

Where δ_{them} is the thermal penetration depth, a the thermal diffusivity, k the thermal conductivity, c material specific heat capacity, ρ material density and t_i the interaction time.

When a laser interacts with materials, two cases warrant closer examination as shown in Fig.2.8:

In the case of $l_{opt} \ll l_{th}$ (typically for metals), the thermal penetration depth is dominant over the effective penetration depth. Temperature at the surface can be calculated as [53]:

$$T = \frac{AI_0 w_b}{\sqrt{2\rho a c}} \arctan \frac{\sqrt{8at}}{w_b} \quad (2.14)$$

where T is the surface temperature of sample, a the thermal diffusivity, ρ the mass density, c the specific heat capacity and t is the time.

For $l_{opt} \gg l_{th}$ (typically for polymers), the effective penetration depth is dominated by optical penetration depth. Their optical penetration depth is much larger than the heat penetration depth as depicted in Fig.2.8 [54].

Fig. 2.8 Left: optical penetration depth is smaller than heat penetration depth; right:

optical penetration depth is greater than heat penetration depth. L=laser beam.

MS=metal sample, OPD = optical penetration depth, HDP=heat penetration depth,

PS=polymer sample [54].

As previously stated, ultrashort pulsed laser material processing is complex. Xiao et al. [53] gave a simple model for calculating the penetration depth of metals by applying two temperature models (TTM). They defined the effective thermal penetration depth as a combination of optical penetration depth and thermal diffusion depth [54],

$$l_{eff} = l_{opt} \oplus l_{th} \quad (2.15)$$

For metals, $l_{opt} \ll l_{th}$. For short pulsed lasers such as nanosecond lasers, the effective penetration depth can be calculated as [54]:

$$l_{eff} \approx \sqrt{2\alpha\tau_p} \quad (2.16)$$

When ultrashort pulsed lasers interact with metals, electrons play an important role on heat transportation. The thermal penetration depth is mainly depending on electrons energy transfer. By applying TTM, the effective thermal penetration depth can be calculated as [54]:

$$l_{eff} \approx \left(\frac{128}{\pi}\right)^{1/8} \left(\frac{k_e^2 C_l}{C_e T_m g^2}\right)^{1/4} \quad (2.17)$$

While for wide bandgap and transparent materials such as polymers, $l_{opt} \gg l_{th}$. The absorbed laser energy is more appropriately treated as a heat source. The effective thermal penetration depth is determined by both optical penetration depth and thermal diffusion length [53].

2.3 Absorption coefficient determination

2.3.1 Background

As discussed in section 2.2.1, photon absorption is the first step of laser-material interaction. Absorption coefficient is an important parameter that determines how much the energy can be absorbed during laser material processing. For linear absorption, the relationship between light absorption and depth of propagation may be written as [46]:

$$\frac{dI}{dz} = -aI \quad (2.18)$$

where I is the light intensity, a the absorption coefficient, z the light propagation depth. Solving equation 2.18 will result in equation 2.2, which is the famous Beer-Lambert law. With equation 2.2, the linear absorption coefficient can be easily determined.

For nonlinear absorption, the relationship is much more complicated. For simplification, second order absorption was considered first in most of the cases [17, 22, 23, 25, 55]. It can be described by:

$$\frac{dI}{dz} = (\alpha + \beta I)I \quad (2.19)$$

Where β is the nonlinear absorption coefficient. As described in equation 2.19, the absorption is a function of the laser intensity. In contrast, for linear absorption, the absorption is always the same at different laser intensity. Determination of the nonlinear absorption coefficient is much more complicated than that of the linear absorption coefficient especially for a Gaussian distributed laser beam. Z scan technique is a simple and an efficient method for the determination of the nonlinear absorption coefficient. The technique is reviewed and discussed in section 2.3.2.

2.3.2 Z scan technique

Z scan technique was first introduced by Mansoor Sheik-bahae et al in 1989 [55]. It is a simple and efficient method that can be applied to determine the nonlinear refraction and nonlinear absorption of material. Fig.2.9 shows a typical “closed aperture” experiment set-up for the z scan technique. “closed aperture” set-up is used to determine the nonlinear refraction of material. For a “thin” film, as the sample moves along the z direction, for example from $-z$ to $+z$ direction, the film reacts as either a positive or a negative focal lens, thus the energy received at the detector is varied. A curve of the z position vs normalized transmittance can be obtained. Fig.2.10 shows a typical “closed aperture” z scan curve. With this curve, the nonlinear refraction can be determined. An “open aperture” experiment set-up is

used to determine the nonlinear absorption of material. For an “open aperture” set-up, the aperture is removed and the detector can receive all the power passed through the material. Thus the influence of material refraction was deducted. Nonlinear absorption can be determined in this arrangement. As the sample moves along the z direction, the power received by the detector is varied due to the nonlinear absorption. Fig. 2.11 shows a typical “open aperture” z scan curve. The nonlinear absorption can be determined with this curve.

Fig. 2.9 A typical “closed aperture” experiment set-up for z scan technique [56].

Fig. 2.10 A typical “closed aperture” z scan curve for nonlinear refraction determination. The normalized transmittance (TR) was measured at different z position [56].

Fig. 2.11 A typical “open aperture” z scan curve for nonlinear absorption determination. The normalized transmittance (TR) was measured at different z position [56].

After the introduction of z scan technique by Mansoor Sheik-bahae et al in 1989, it becomes a popular and generally used method for the measurement of material nonlinear properties. It has been used to measure the nonlinear properties of polymers [16, 19], glasses [14, 18, 20, 21, 24], semiconductors [17, 22, 23, 25] and organics [15, 26] with the laser time-scale varied from millisecond to femtosecond.

Serna et al. has investigated the nonlinear optical properties of cuprous oxide by applying the z scan technique [57]. Cuprous oxide is a widely used p-type oxide semiconductor. A 450 μm thick cuprous oxide sample was used in the experiment. A Ti:sapphire based fs laser was employed in the experiment with a pulse width of 65 fs. The open-aperture z scan curve was obtained. The nonlinear absorption

coefficient was measured to be 6.6 cm/GW and 5.0 cm/GW at the wavelength of 790 nm and 1064 nm respectively.

Smith et al. has investigated the nonlinear absorption of a thin gold film [58]. A Nd:yttrium–aluminum–garnet laser was used in the experiment. The pulse width is 30 ps with a laser wavelength of 532 nm. The sample thickness is 50 Å. The transmitted power at different position z was measured. The nonlinear absorption coefficient was measured to be in the range of 1.9×10^{-3} to 5.3×10^{-3} cm/W.

It is to be highlighted here that the z scan experiment should be carefully conducted. Unsuccessful control of the experiment parameters such as the sample thickness, beam quality and fluctuation of laser power may induce an inaccurate result [56].

There is a limitation of the z scan method. The sample thickness should be much less than the Rayleigh range of the laser in order to get an accurate result. This is because the analysis is based on a thin film assumption. Thus, most of the previous works only focused on the nonlinear property investigation of thin samples. Mansoor Sheik-bahae himself also discussed this limitation in [59]. The analysis of a thick sample is much more complicated compared with a thin sample. Hermann and McDuff [60] and Zang [61] have provided an analytical solution of the z scan technique for the thick samples. In their analysis, the thick sample is treated as a stack of thin layers and the beam shape was assumed to be constant.

2.3.3 Limitation of previous works

Z scan technique is a simple and efficient technique for the determination of the nonlinear properties of material. However, the technique is only applicable to a thin

sample with thickness less than the Rayleigh range. The analysis for a thick sample is much more complicated, and there are few works on thick sample analysis. Although Hermann and McDuff [56] and Zang [61] have derived an analytical solution of the z scan technique for thick samples, its applicability has not been examined and analyzed experimentally.

2.4 Thermal effects

2.4.1 Thermal effects induced by ultrashort pulsed laser

The pulse duration of an ultrashort pulsed laser is so short that there is insufficient time for the transfer of laser energy by conduction to the substrate material over the pulse duration. As such, traditionally, it was believed that there are no or negligible thermal effects for ultrashort pulsed laser-material interaction. However, it was demonstrated recently that over a longer time duration than the pulse duration, thermal effects for ultrashort pulsed laser-material interaction is significant, and was observed in ultrashort pulsed laser-induced phase transformation of metals [32, 33] and semiconductors [62, 63]. Indeed, significant thermal effects of femtosecond irradiation on dielectrics [34], semiconductors [35] and metals [36, 37] have been observed directly.

Time for electrons transferring energy to phonons is called electron-phonon coupling time. The electron is excited almost instantaneously on laser irradiation. The thermalization of electron is on a time scale of ~ 100 fs [11]. At this time scale the lattice remains “cold”, since the electron-phonon coupling time is in the order of picosecond [64]. As such, an ultrashort pulsed laser is loosely defined as a laser

with a pulse duration less than a few picoseconds [64-66]. After the electron-phonon coupling time, the lattice is heated up as shown in Fig.2.12.

Fig. 2.12. Simulation of electron and lattice temperature by applying two temperature model (TTM), copper was irradiated with laser pulses ranging from 50 fs to 500 ps [64].

Ladieu et al. has shown that the temperature at the center of crater during ultrashort pulsed laser-material interaction was more than 3000°C. By depositing a series of micro-thermocouples onto a quartz sample surface, heating at 50 μm away from the laser impact location at millisecond scale was measured. Heat propagation equation and Helmholtz equation were applied to estimate the minimum temperature at the crater center [34]. Their conclusion was that thermal effect is significant.

Vorobyev et al. has investigated the thermal effects of femtosecond laser by employing a calorimetric method [67]. The energy residual on the sample following laser ablation was measured. Their result shows that a significant amount of energy was deposited onto the sample surface after laser irradiation.

Ultrashort pulsed laser-induced phase transformation of metals has been reported by several groups. For example, Yoichi et al. reported that by ablating copper with femtosecond laser, the surface crystallinity was partially changed to amorphous. The material crystallinity is measured by x-ray diffraction (XRD). The thickness of HAZ is around 0.5-3.5 μm [32]. Ultrashort pulsed laser-induced phase transformation of semiconductors has been intensively studied, such as ultrashort pulsed laser-induced crystallization of hydrogenated amorphous silicon [68]. The crystallization is studied by Raman spectra analysis. Femtosecond laser has been reported to induce phase transformation of InSb surface [62], crystallization of amorphous N:GeSb film and amorphous Si₂Sb₂Te₃ film [69]. The phase transition can be studied by coherent phonon spectroscopy [70].

Temperature measurement during laser material processing is a direct method to study thermal effects of ultrashort pulsed laser. Tran et al. studied the thermal effects of femtosecond laser on silicon and metals by employing an infrared camera [35-37]. Temperature was captured during laser material processing. Their result shows that more than half of the laser energy was deposited onto the sample and was subsequently conducted as heat into the sample.

2.4.2 Simulation of laser-induced heat conduction

Simulation is an indirect but efficient method to study the temperature increase during laser material processing. Measuring the temperature during laser material processing is rather challenging, and is not always possible and applicable, especially for the polymers. There are various research works on the simulation of heat conduction during laser-material interaction [71-80]. The heat conduction simulation has been conducted for different applications such as temperature increase investigation [71, 81], laser melting [75, 77], laser joining [76] and surface structure modification analysis[73].

Bachy et al. has simulated the temperature increase of a polymer (VESTAMID® HTplus TGP3586) irradiated by a Nd:YAG laser. A 3D FE model was employed using the commercial software ANSYS [73]. The laser incident power was set to be the input heat source with a Gaussian distribution. A moving heat source was simulated as shown in Fig.2.13. For having the incident power as the input heat flux, the implicit assumption is that all the laser power is absorbed and converted to heat. This assumption is not quite appropriate as not the energy will be absorbed as the absorption coefficient will be less than unity, and there will also be reflection on the surface.

Fig. 2.13 Simulated temperature profile of polymer at different laser power: (a) 8W and (b) 12 W at 0.0195s with a scanning speed of 300 mm/s [73] .

Laser heating can be applied as an earlier step to enhance material cutting. The cutting force can be reduced with the decreased material strength due to heating. A 3D numerical model developed by UPV/EHU was employed by Arrizubieta et al. to predict the temperature increase of the material before the cutting tool [71]. In this model, the laser power was treated as an input heat source. Only linear absorption was considered and the absorptivity was set to be 0.76. Since the laser details were not presented in the paper, the appropriateness of the simulation cannot be assessed.

Kappes et al. has simulated the temperature increase of laser heated polymer in microsecond time scales. A 810 nm diode laser with pulse duration of 15 μ s was employed. A 3D FE model using Comsol Multiphysics has been employed to simulate the temperature changes during laser material processing. Since the material is transparent to the laser wavelength, an organic NIR-dye was added into the material to enhance the absorption. The absorptivity was measured by using a photosepectrometer. The input laser power is treated as a heating source by applying the Beer-Lambert law [72]. The linear absorption coefficient was set according to the measured absorptivity.

Research has been conducted on the simulation of temperature increase of human iris with femtosecond laser irradiation [78, 82]. A fs laser with a pulse duration of 60fs was employed. The central wavelength is 1053 nm with a repetition rate of 60 kHz. The results of the 2D FE model simulation of the temperature increase during femtosecond laser iris interaction by Sun et al. [78] is shown in Fig. 2.14. The input laser power was treated as the heating source with the application of the Beer-Lambert law. The absorptivity and reflectivity is measured by employing a photospectrometer. The implicit assumption is that only linear absorption occurred and all absorbed energy has been converted to heat dissipating into the bulk material. This assumption has not been verified, and is not likely to be valid. Nonlinear absorption should be considered during ultrashort pulsed laser-material interaction.

Fig. 2.14 Simulated temperature distribution of retina sample irradiated with 60 fs laser at 1 μJ laser pulse energy. Inset: maximum temperature of the retina as a function of time calculated from the model [78].

2.4.3 Limitation of previous works

Previous studies have shown that ultrashort pulsed laser induced thermal effects are significant. Different methods were applied to investigate this phenomenon, including temperature measurement by micro-scale thermocouples, calorimetric method and temperature measurement by infrared camera. Temperature measurement by infrared camera during laser material processing is a direct method to study the thermal effects; previous studies only focused on metals and semiconductors. Ultrashort laser induced thermal effects on polymers is seldom investigated. The thermal effects induced by ultrashort pulsed laser via nonlinear absorption are yet to be systematically investigated.

In most of the previous works for heat conduction simulation, the laser power was treated as either a constant heat flux or heat source, with or without the

consideration of the absorption coefficient to account for the laser power absorbed by the material; for those considered the power absorbed by the materials through the absorption coefficient, often Beer-Lambert law is employed, implying that non-linear absorption is ignored. For continuous wave lasers and long pulsed lasers this assumption is valid. However, for ultrashort pulsed lasers, nonlinear absorption must be considered as this is the dominant mechanism, and that the absorption changes with the laser intensity. This is especially important for polymers which are transparent to the laser wavelength at low laser intensity, i.e. there is negligible linear absorption. With transparent materials such as polymers, the laser can focus within the material. Hitherto, there is yet any comprehensive simulation, with experimental validation, on nonlinear absorption which is a function of laser intensity, and the effect of the focusing location of the laser beam.

2.5 Surface wettability modification

2.5.1 Background

Surface wettability is one of the primary surface properties of solid materials [83]. Controlled modification of polymer surface wettability, to either hydrophilic or hydrophobic, is highly desirable for various applications. For example, superhydrophobic surfaces are well suited for self-cleaning of contaminations. Surface wettability also determines the reagent flow behavior in microfluidic channels, and ease of adhesion of cells. Highly hydrophilic surface can improve surface adhesion and wettability, a desirable characteristic for coating and joining applications. High wettability contrast surface could be employed to confined inkjet droplets to hydrophilic region and avoiding hydrophobic region, with the potential

of having printed line-width less than the droplet diameter. Indeed, surface modification of polymer materials has received much attention and has been widely investigated recently [5, 6, 38, 39].

Different techniques can be employed to modify polymer surface wettability, which include wet-chemical etching [84], corona discharges [85], plasma treatment [86, 87], ion beam treatment [88, 89], electron beam irradiation[90], and laser irradiation method. Compared with other methods, laser irradiation, being a fast and clean process, has a number of unique advantages. These include its non-contact property, highly selective and localized treatment, precise control for producing complex features, and having minimal effect on the bulk material. Laser irradiation has been applied for surface modification of metals, polymers and semiconductors [9, 39-43, 91]. Ultrashort pulsed lasers are increasingly used as a tool for surface treatment. In contrast to long-pulsed lasers, ultrashort pulsed lasers can induce nonlinear absorption of photons and has minimum thermal effect. In addition, the use of ultrashort femtosecond laser pulses allows the treatment of features with precision, as the laser beam can be accurately positioned and tightly focused into a spot size of several microns.

Contact angle (CA) measures the degree of wetting of a liquid droplet on a solid surface, and thus the hydrophilicity/hydrophobicity of surfaces. The classification of hydrophilicity/hydrophobicity is shown in Fig.2.15. Droplet forms a spherical shape at high contact angle, and the contact between droplet and surface is small. While at low contact angle, the droplet spreads over the surface and wets more area [92]. Superhydrophobic surface with low sliding angle has self-cleaning properties [93].

Fig. 2.15 Four classes of surface wettability [92].

Contact angle on a solid surface is determined by the interfacial tensions between liquid-air, solid-liquid and solid-air, which can be described by Young's equation (or Young contact angle (YCA)):

$$\gamma_{SA} - \gamma_{SL} = \gamma_{LA} \cos \theta \quad (2.20)$$

Where γ_{SA} , γ_{SL} and γ_{LA} are solid-air, solid-liquid and liquid-air interfacial tensions respectively. θ is the contact angle as shown in Fig.2.16.

Fig. 2.16 Wettability of solid surface [92].

YCA is developed for an ideal smooth, rigid, chemically homogeneous, insoluble and non-reactive surface. As such, YCA is the ideal contact angle.

In practice, most of the surface is rough, heterogeneous and reactive. The equilibrium wetting of a rough surface had been studied by Wenzel [94] and Cassie and Baxter [95]. The effect of roughness on CA can be expressed by Wenzel's equation:

$$\cos \theta_w = r \cos \theta_Y \quad (2.21)$$

where θ_w is the actual contact angle, θ_Y the YCA, r the roughness ratio between the actual and projected solid surface area. r equals to unity for a smooth surface, and is larger than unity for a rough surface. According to Wenzel's equation, roughness amplifies the wettability of a material surface. This implies that with increasing surface roughness, a hydrophilic surface will become more hydrophilic and a hydrophobic surface more hydrophobic. The assumption of the Wenzel's equation is that liquid penetrates completely into the rough grooves, i.e. homogeneous wetting.

However, on a rough surface, sometimes the droplet cannot completely wet the surface. Air bubbles may be trapped in the grooves under the liquid as shown in Fig.2.17. This is considered as heterogeneous wetting (chemically heterogeneous) [96]. An equation developed by Cassie and Baxter describes this wetting behavior by considering air as the second chemistry. The transition between the Wenzel and Cassie-Baxter regimes plays an important role for superhydrophobic surface owing to the reduction of solid-liquid contact area [92]. The Cassie-Baxter equation [95] can be described as:

$$\cos \theta_{CB} = fr \cos \theta_Y - (1 - f) \quad (2.22)$$

Where θ_{CB} is the actual contact angle, θ_Y the YCA, r the roughness ratio and f the fraction of projected area wetted by liquid.

Fig. 2.17 Wetting on rough surface, a) homogeneous wetting, liquid penetrates into grooves, b) heterogeneous wetting, air bubbles trapped in grooves under liquid [96].

CA is only used to characterize the static wetting behavior. To explain the sticking behavior of droplet, contact-angle hysteresis (CAH) can be employed. CAH is defined as the difference between the advancing and receding angles of a moving or evaporating droplet as shown in Fig.2.18 [92].

$$CAH = CA_{adv} - CA_{rec} \quad (2.23)$$

Fig. 2.18 Sliding angle and hysteresis [92].

The ease of a droplet sliding over a surface can be characterized by its sliding angle. Sliding angle is the angle upon which droplet starts to move. For instance, a water droplet starts to roll off on a water repellent solid surface when it tilts to a certain angle. This angle is the sliding angle. Self-cleaning surface has low sliding angle ($<10^\circ$) [92].

2.5.2 Laser parameters affecting surface wettability

Laser induced surface wettability modification has been intensively studied. Different laser parameters have different effects on surface structure and surface chemistry. The surface structure and surface chemistry further affect surface wettability. In this section, the major parameters having an effect on surface wettability are reviewed, which includes laser fluence, number of pulses, energy deposition rate and total energy.

2.5.2.1 Laser fluence

Laser fluence can be described as energy per unit area, is an important parameter that affects surface wettability. It can be calculated as [1]:

$$F = \frac{E_{pulse}}{\pi w_o^2} \quad (2.24)$$

where F is the laser fluence, E_{pulse} the pulse energy and w_o the beam radius.

Oliveira et al. showed that laser fluence has an effect on the induced microstructures when polyimide surfaces were treated with a 248 nm KrF laser (pulse duration of 30 ns) [40]. As the fluence increased, the size of microstructure was increased. The

increased microstructure further affected the wettability. Direct relationship between laser fluence and surface water contact angle is shown in Fig 2.19.

Fig. 2.19 Water contact angle of polyimide surface at different laser fluence [40].

2.5.2.2 Number of pulses

Another important parameter which has an effect on surface wettability is the number of pulses. Laurens et al. irradiated PEEK surface with excimer lasers (193 nm ArF laser with pulse duration of 20 ns or 248 nm KrF laser with a 30 ns pulse duration). They showed that as the number of laser pulses increased, the surface water contact angle increased [97]. Rytlewski et al. investigated the effect of number of pulses on surface wettability of polylactide by employing a 193 nm ArF excimer laser (pulse duration of 20 ns) [98]. Their result shows that the number of laser pulses had effects on both surface chemistry and surface structure. The direct relationship between surface water contact angle and number of pulses is shown in Fig.2.20.

Fig. 2.20 Water contact angle of polylactide surface at different number of pulses [98].

2.5.2.3 Energy deposition rate and total energy

As discussed in section 2.5.2.1 and 2.5.2.2, both laser fluence and number of pulses (which is determined by the scanning speed) have an effect on surface wettability. Wang et al. [13] investigated the combined effect of both parameters on surface wettability through the energy deposition rate parameter, which measures the energy deposition on surface per unit area per second. The effect of total energy irradiated onto the sample surfaces on surface wettability was also discussed. For multiple scanning, the effect of the distance between scanned lines, i.e. the shifting pitch should be considered. By employing the energy deposition rate and total energy, the combined effect of three parameters, namely fluence, scanning speed and shifting pitch, can be taken into consideration. Fig 2.21 shows the effect of energy deposition rate and total energy on PMMA surface by varying the laser fluence. A femtosecond laser with pulse duration of 150fs and wavelength of

775nm was employed for their experiments. When the total energy was less than 1000 J/cm², WCA increased as thermal deposition rate and total energy increased. When the total energy was above 1000 J/cm², WCA decreased as thermal deposition rate and total energy increased.

Fig. 2.21 Water contact angle at different energy deposition rate and total energy irradiated onto the surface. Energy deposition rate is varied by laser fluence [13].

2.5.3 Laser-induced surface wettability modification

2.5.3.1 Surface characteristics affecting wettability

Laser-induced surface modification of metals, polymers and semiconductors [9, 39-43, 91] has been intensively studied. Rytlewski et al. has investigated surface modification of PS by employing a 193 nm ArF excimer laser (pulse duration of 20 ns). WCA varies from 107° to 100° as a result of changing surface carbon oxygen ratio [45]. Bagheri-khoulenjani et al. also studied the surface modification of PS induced by ArF excimer laser and plasma treatment. Their results demonstrated that by laser irradiation, surface wettability can be modified to 70° and 100° from the

original WCA of 88° [44]. The changing of WCA was due to modification of surface structure at different number of laser pulses.

The wettability of the resulting surface is determined by surface chemistry and surface structure [99]. Laser irradiation on polymer surface not only induces photo-oxidation, photo-crosslinking, photochemical reactions but also changes of surface structure [100]. Hence, by controlling the laser irradiation process, both the surface chemistry and surface structure (including micro- and nano-scale structures) can be modified to obtain the desired surface wettability.

a) Surface structure

Surface structure is a crucial factor on surface wettability, and has been widely investigated. PODR1 polymer film was fabricated with squared shaped pillar morphology as shown in Fig.2.22, after which the film was coated with (heptadecafluoro-1,1,2,2-tetrahydrodecyl) trichlorosilane for 24 hours in a low pressure chamber. The water contact angle of the surface obtained is 157° as shown in Fig.2.23. Compared to a pristine flat surface coated with (heptadecafluoro-1,1,2,2-tetrahydrodecyl), the WCA was increased by approximately 50° [101]. Thus, it is inferred that the wettability was increased by 50° due to the change in surface structure.

Fig. 2.22 a) AFM image of the microstructured PODR1 film surface. (b) Cross-section analysis of the microstructured region along the red dotted line in (a)[101].

Fig. 2.23 Water droplet on PODR 1 a) untreated surface and b) microstructured surface treated with fluorosilane [101].

Another polymer example of surface structure on wettability is polyimide. Different surface structure was produced with KrF laser ablation. Different conical featured morphology was created by varying the laser fluence. The wettability of polyimide surface was determined by the conical featured morphology [40]. As the laser

fluence increased, both the apparent contact angles of the homogeneous regime (because of increased cone dimensions) and heterogeneous regime (because of increased cone distance) increased. Maximum WCA 162° was achieved at fluence of 155 J/cm^2 [40]. The WCA measured at 1 J/cm^2 showed that the WCA increased from 75° to 105° due to the chemical changes [40]. The chemical changes did not account entirely for the large change observed since the maximum WCA was 162° . The contact angle increment due to the change of surface structure was approximately 47° [40].

The effects of micro-scale structure and nano-scale structure have also been discussed. An ultralow hysteresis superhydrophobic surface (maximum WCA 165 ± 1.4) of SU-8 was achieved by using excimer lasers to create dual micro/nanostructures on the surface [38]. It was shown that the ultralow hysteresis was mainly due to the presence of nanoscale debris rather than microscale debris, see Table 2.2.

Table 2.2 Overview of sample surfaces, water contact angles and hysteresis result [38]

surface	microstructure present	nanoscale debris present	water contact angles, deg		hysteresis, deg
			θ_{adv}	θ_{rec}	
1 ^b	no	no	$118.6 \pm 1.75^\circ$	$80.5 \pm 1.05^\circ$	$38.1 \pm 2.04^\circ$
2.	yes	no	$164.1 \pm 1.50^\circ$	$136.3 \pm 1.68^\circ$	$27.8 \pm 2.25^\circ$
3.	yes	yes	$165.0 \pm 1.40^\circ$	$164.3 \pm 1.89^\circ$	$0.7 \pm 2.35^\circ$
4.	no	yes	$164.2 \pm 1.50^\circ$	$164.8 \pm 1.83^\circ$	$-0.6 \pm 2.37^\circ$

Weibel et al.[102] demonstrated a different result. Aluminium substrate's wettability is modified with trimethoxypropylsilane dipping and coating with a thin

perfluorinated layer. The aluminium substrate is micro or/ and nanotexturized before silane and PTFE treatment as presented in Fig.2.24. It shows that the surface structure and surface chemistry both contribute to the resulting superhydrophobic surface. Surface wettability is influenced by both micro-scale and nano-scale structures. As presented in Fig.2.24 (b), (c), (f), and (g), the influence of microstructure on wettability seems more significant as compared with nanostructure. Comparing Fig.2.24 (a), (b), (c), (d) with Fig.2.24 (e), (f), (g), (h), surface wettability is also influenced by surface chemistry significantly particularly in the case of a flat surface.

Fig. 2.24 Images of static water contact angle showing the effect of chemical functionalization and micro/nanostructure on surface hydrophobicity [102].

Continuous wave laser has also been employed for the surface wettability modification of polymers. Waugh et al. has investigated the surface wettability modification of nylon 6,6 by using a continuous CO₂ laser and a 157 nm F₂ excimer

laser (pulse duration of 11 ns). Groove patterns were formed on the sample surface with laser irradiation. Under CO₂ laser irradiation, the material is melted and re-solidifies on the surface and thus the groove patterns were formed. However, the formed groove patterns were not as clear as that created by F₂ laser, see Fig. 2.25 and Fig. 2.26. Thus, the excimer laser has an advantage on high precision and accurate control of the created structure. In recent research works, excimer lasers, picosecond lasers and femtosecond lasers are more generally used in laser polymer processing. With grooves created by CO₂ laser, the surface WCA increased to 52.36° from the original 49.34°. In contrast, with grooves created by F₂ laser, the WCA increased to 72.92° [103]. Instead of surface chemistry, the created surface structure has been shown to be the main factor dominating the surface wettability.

Fig. 2.25 Surface profile of continuous CO₂ laser treated nylon 6,6 at 5W [103].

Fig. 2.26 Surface profile of F2 excimer laser treated nylon 6,6 at fluence of 40 mJ/cm² [103].

b) Surface chemistry

Surface chemistry is another important factor that determines surface wettability. It is known that oxygen-containing groups on polymer surfaces, such as C-O, C=O, and O-C=O, are responsible for the change of surface hydrophilicity[104]. As the polarity of C=O bond is more intense than that of C-O bond, C=O double bond is most important for the hydrophilicity of polymer surfaces. Laser-assisted wettability modification of polymers (such as PMMA, polyimide, polylactide) through inducing chemical reactions on the surface has been reported [6, 40]. O'Connell's group showed that polymers' (LDPE, UHMWPE, sarlink N12 and PCL) wettability can be modified to be more hydrophilic by irradiating a 172 nm UV light on sample surface. A 58° water contact angle of both LDPE and UHMWPE was achieved after

20 min treatment due to the increasing oxygen polar groups formed on the surface. Pristine water contact angle of LDPE and UHMWPE was 92° and 102° respectively [105]. Table 2.3 shows an example of PMMA treated with femtosecond laser [6]. By varying the laser fluence, the surface polar and nonpolar groups can be changed. The increase of wettability is due to the increase in surface polar groups. For instance, at high laser fluence of 52.7 J/cm², the polar groups increased to 68.84% from the original 45.9%, the WCA decreased to be around 0° from the original 76°. While at low laser fluence of 0.4 J/cm², the polar groups decreased to 39.78%, and the WCA increased to 125°.

Table 2.3. Relative amount of oxygen/carbon functional groups (at. %)

	Chemical bond	Raw PMMA	High fluence (52.7 J/cm ²)	Low fluence (0.40 J/cm ²)
Nonpolar groups	C 1s C-H	40.25	29.78	39.88
	C 1s C-C	13.84	1.38	20.35
	Sum	54.09	31.16	60.23
Polar groups	C 1s C-O	13.44	10.97	10.85
	C 1s O-C=O	10.39	6.38	8.07
	O 1s O=C	11.43	29.99	11.57
	O 1s O-C	10.64	21.50	9.28
Sum		45.90	68.84	39.78

To control surface wettability, chemical reaction during laser treatment should be controlled. Wettability modification of polymers with lasers under different atmospheres has been studied. For example, He et al. investigated the wettability modification of poly(ϵ -caprolactone) by femtosecond laser irradiation (pulse duration of 150 fs) under different ambience, namely air, O₂ and CF₄ [106]. Wettability increased with increased oxygen-containing groups on the surface. Under the same laser parameters, the water contact angle of the sample decreased the most (70°) at oxygen ambience comparing to the sample under air (90°) and CF₄

(117°) gas atmosphere. This was due to the oxidation of the sample surface. The investigation also showed that as laser power increased, the WCA decreased in air, O₂ and CF₄ [106]. This was due to the increasing oxidation on the polymer surface. It has been founded that the water contact angle of a hydrophilic surface tends to restore its original untreated value over time in open air after treated with different methods such as laser treatment, chemical treatment, and plasma treatment [105]. This phenomenon is called hydrophobic recovery. Connell et al. reported that LDPE, UHMWPE, Sarlink and Nylon 12's surface water contact angle increased over time after treated with 172 nm UV light [105]. For instance, LDPE's surface water contact angle was modified to 51° from the pristine 78° after UV treatment. However, after 14 days, the water contact angle of treated LDPE increased to 70°. The carbon content of treated LDPE, Sarlink and Nylon 12 were increased over time while the oxygen content decreased over time. The increased water contact angle was due to the decreased polar groups formed on the surface caused by the reaction between surface and air.

2.5.4 Limitation of previous works

Studies on laser induced surface wettability modification show that surface structure and surface chemistry are the main factors that determines the surface wettability. However, the conditions for the relative dominance of these two parameters are not entirely clear. Some research works have shown it is the surface structure dominating the surface wettability, while others have shown it is the surface chemistry dominating the surface wettability; there are investigations indicating that both surface structure and chemistry are important on surface wettability. Thus,

there is a need to investigate the effect of these two parameters on polymers' surface wettability.

Polystyrene is a widely used thermoplastic polymer in microfluidic and biological devices. Polystyrene is transparent and rigid, with high electrical and thermal insulation [45]. It is also widely used in our lives such as packaging, bottles, trays, lids and containers. It has good resistance to alcohols, concentrated acid, alkaline and polar solvent [107]. The pristine static water contact angle (WCA) of PS is measured to be around 88.2°. Hitherto, there is only limited investigation on laser-induced surface modification of PS. The modified surface WCA was in a small range and the transparency after laser treatment is not discussed. The structure created by laser is in micro-scale and without controlling the structure created.

2.6 Summary

Ultrashort pulsed laser-material interaction is complicated as compared with long pulsed lasers and continuous wave lasers. In this chapter, the basic concepts including photon absorption, ablation and penetration depth have been introduced. Photon absorption is the first step of laser-material interaction. For ultrashort pulsed laser, nonlinear photon absorption is the dominant absorption mechanism. Z scan technique is a simple and efficient method for the determination of the nonlinear absorption coefficient. As this technique is limited to thin samples, most of the previous works only focused on thin samples (sample thickness less than the Rayleigh range). The analysis of thick samples is much more complicated; Hermann and McDuff [60] and Zang [61] have derived an analytical solution of the

z scan technique for thick sample. However, the applicability of the z scan technique for a thick sample is yet to be examined and analyzed experimentally.

Heat conduction and thermal effects are important as they have effects on the machining precision and material property after laser treatment. The thermal effect of ultrashort pulsed laser is significantly less as compared to long pulsed laser and continuous laser. However, as discussed in section 2.4, the thermal effects of ultrashort pulsed laser are still significant, with a significant percentage of laser energy being conducted into the materials. Hitherto, the understanding remains lacking on the thermal effects of ultrashort pulsed laser processing of polymers.

Simulation is an indirect but efficient method to study the temperature increase during laser material processing. Measuring the temperature during laser material processing is challenging. In most of the previous works for heat conduction simulation, the laser power was treated as either a constant heat flux or heat source, with or without the consideration of the absorption coefficient to account for the laser power absorbed by the material. The implicit assumption is that the absorption is through linear absorption, with nonlinear absorption ignored. For continuous wave lasers and long pulsed lasers, this assumption is valid. However, in the interaction of ultrashort pulsed laser and material, nonlinear absorption must be considered as this is the dominant mechanism, and that the absorption changes with the laser intensity. Hitherto, there is yet any comprehensive simulation, with experimental validation, on nonlinear absorption which is a function of laser intensity.

Laser induced surface wettability modification has been intensively studied. Surface structure and surface chemistry are the main factors that determine the surface wettability. The conditions for their relative dominance on surface are yet to be investigated or understood. Investigations on laser-induced surface modification of polystyrene (PS) is quite limited, with the modified surface WCA restricted in a small range. As PS is a widely used thermoplastic polymer which finds applications in microfluidic, biological devices and life sciences, there is merit to investigate if the WCA of PS could be varied over a much larger range through laser irradiation.

Chapter 3 Thermal imaging and temperature measurement

In this investigation, temperature during laser polymer processing has been directly measured by an infrared camera. Infrared camera temperature measurement is a noncontact method. Compared with a contact method, an infrared camera can measure the surface temperature over an area with minimum interference of the measured temperature field. The response time of an infrared camera is also much faster than a contact method [108]. It has also been demonstrated that an infrared camera is suitable for measuring the surface temperature field of an object during laser processing [35-37].

Infrared camera measures the temperature of an object through measuring its thermal radiation, which can be from a variety of sources. These include the radiation of object itself, the radiation from the atmosphere, the radiation from the camera components, and the radiation reflected from the surroundings [108]. The radiation from the atmosphere is quite small since infrared camera works in infrared atmospheric window [108]. The radiation from the camera components is compensated by the camera calibration [108]. The radiation due to different material emissivity and reflection from the surroundings have to be separately calibrated.

Since a material is generally not a black body (with emissivity of unity), different material has different emissivity. Different surroundings also have different radiation characteristics. Thus, the proper calibration of infrared camera is required for accurate temperature measurements.

The calibration of infrared camera for temperature measurements could be achieved by measuring the temperature of a sample by both the infrared camera and thermocouples simultaneously. Temperature measured by thermocouples will be used as the reference temperature for calibration. Since thermocouple measures temperature directly, its measurements are not affected by the differences in radiation. By taking proper precautions, the measured temperatures by thermocouples can be close to the physical temperatures. The temperature measuring method and errors by infrared camera and thermocouples are introduced in the subsequent sections, which are followed by the calibration procedure.

3.1 Temperature measurement by infrared thermal camera

3.1.1 Working principles of infrared thermal camera

Infrared was discovered by William Herschel in 1800 and the law of radiation is described by Max Planck in 1900 [109, 110]. After fifty years, the first infrared camera was developed. Infrared camera detects infrared radiation from an object. Any objects with a temperature above absolute zero (-273.15°C) will emit electromagnetic radiation. The emission of an object is directly related to the temperature of the object [109]. Thus an infrared thermal camera can be employed for temperature measurement by converting the measured radiation to temperature. The electromagnetic waves can be classified into different regions according to the wavelength of radiation. Infrared (IR) is electromagnetic radiation with wavelength ranges from 700 nm to 1 mm, see Fig.3.1.

Fig. 3.1 Electromagnetic spectrum [111].

The infrared energy emitted by an object will be absorbed by the atmosphere and will have an effect on the accuracy of the temperature measurement. To minimize this effect, infrared thermography normally operates in the wavelengths from 3 -5 μm and 8 – 14 μm, which fall in the infrared atmospheric window [108]. At the infrared atmospheric window, the atmosphere is rather transparent to the radiation, and without intermediate absorption and re-emission as depicted in Fig.3.2. To increase the radiation signal detected, a camera with a shorter wavelength should be used. However, as the laser of interest has a wavelength of 750 nm, it will be prudent to choose an infrared camera operating at a wavelength away from the laser wavelength to avoid any accidental laser damage to the camera. By considering these two factors, A SC5000 infrared camera (FLIR) with a working wavelength of 3.7 μm to 5.15 μm is employed to measure the temperature field for the current investigation.

Fig. 3.2 Ground atmospheric IR windows [112].

The emission of an object is determined by its material, color, surface roughness and the temperature. It can be explained by Kirchhoff's law, Plank's law, Wien's displacement law and Stefan-Boltzmann law.

According to Kirchhoff's law, when an object is in thermodynamic equilibrium the emissivity and absorptivity is the same [108].

$$\alpha = \varepsilon \quad (3.1)$$

Both the emissivity and absorptivity will change when the wavelength changes.

The equation can be written as

$$\alpha(\lambda) = \varepsilon(\lambda) \quad (3.2)$$

A black body's emissivity and absorptivity is equal to 1. The emission of a black body at different temperature and wavelength can be described by Plank's law [108]

$$E_{\lambda}(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \quad (3.3)$$

where E is the spectral radiance, T the absolute temperature, k_B the Boltzmann constant, h the Planck constant, and c the speed of light in the medium. The radiation of a black body at different temperature is depicted in Fig.3.3.

Fig. 3.3 Black body radiation of different temperatures at different wavelength [84]

As shown in Fig. 3.3, a body with a higher temperature has higher radiation. The radiation of a black body covers a big part of the electromagnetic spectrum. The peaks are different at different temperatures. As the temperature increases, the peak wavelength emitted by a black body decreases. The peak wavelength can be calculated by Wien's displacement law [108].

$$\lambda_{max} = \frac{b}{T} \quad (3.4)$$

where λ denotes the peak wavelength, b the constant of proportionality with a value of $2898 \mu\text{K}$, T the absolute temperature. This also explains the color change of an object with temperature.

The relationship between temperature and emission is described by Stefan-Boltzmann law [108]. It is a derivation from Plank's law.

$$E = \varepsilon \sigma T^4 \quad (3.5)$$

where E is the energy emitted per unit area per unit time, σ the Stefan's constant and ε the emissivity of an object. A black body's emissivity is equal to 1. Equation 3.5 shows that emission of a body scales to fourth power of temperature, indicating that radiation increases significantly with an increase in temperature.

3.1.2 Radiation measurement by infrared thermal camera

An infrared camera, detecting infrared radiation, may be used for temperature measurement as shown in Fig. 3.4 [113].

Fig. 3.4. Emission received by detector [113].

As depicted in Fig. 3.4, the emissions received by a camera detector include:

1. Emission from the object
2. Emission from the atmosphere
3. Emission from the reflection of the surrounding objects' emission

4. Emission from the camera components

For most cameras, the error caused by emission from the camera components has already been compensated [114]. As an infrared camera operates in the range of infrared atmospheric window, the effect of atmospheric absorption and emission are relatively quite small [114]. As such, only the emission from the object (R_T) and the emission from the reflection of the surrounding (R_{bg}) are of significance [115]. Thus the relationship between the radiation from an object and the radiation detected by an infrared camera can be described as:

$$R'_T = \varepsilon R_T + R_{bg} \quad (3.6)$$

To improve the accuracy and to reduce the environmental effect, a sample surface with low emissivity can be painted black to increase its emissivity. For emissivity close to unity, the value of the first term on the right side of equation 3.6 will be relatively large; the second term will be relatively small, and may be neglected:

$$R'_T \approx R_T \quad (3.7)$$

The errors in temperature measurement by infrared camera [116] may include:

1. Atmospheric attenuation
2. Uncertainty from the infrared camera itself
3. Surrounding's effect
4. Emissivity of the object itself.

As previously discussed, error one is small, unless there are other particles in the atmosphere; thus by having a clean environment, this error will be negligible [116]. The second error is caused by the instrument itself. It is limited by the detector's signal-to-noise ratio, a specific error is in the order of 0.5-2% or better [116]. The errors originated from the object and the surroundings could be minimized by having a high object surface emissivity as discussed. Object surface emissivity could be enhanced by painting the surface with black paint which has high emissivity.

3.2 Temperature measurement by thermocouples

A thermocouple is a temperature measuring device made by two different conductors. The measuring ends of these two conductors are jointed together. The other ends are open, reference ends. When the temperature of the measuring ends and the joint end is different, an electric voltage is generated. The electric signal is converted to temperature by a thermometer. There are many advantages of using a thermocouple for temperature measurement [117]. The thermocouple can be made in different sizes according to the life expectation, response time and drift requirements. A wide range of temperature can be measured, and it is easy to install. The thermocouple is classified into different types according to the conductor combination such as types E, J, K, and M. In this calibration type K thermocouple is selected. Type K thermocouple (NiCr/NiAl) is the most widely used thermocouple. It is inexpensive and can measure temperature ranges from -200°C to 1350°C. Table 3.1 shows the accuracy of type K thermocouples at different temperatures.

Table 3.1 Accuracy of K type thermocouples at different temperature [117].

Actual Temperature, °C (°F)	Maximum Accuracy, ±°C (±°F)
0 (32)	1.1 (2.0)
100 (212)	1.1 (2.0)
200 (392)	1.1 (2.0)
300 (572)	1.2 (2.2)
400 (752)	1.6 (2.9)
500 (932)	2.0 (3.7)
750 (1382)	3.0 (5.4)
1000 (1832)	4.0 (7.2)
1250 (2282)	5.0 (9.0)

When measuring surface temperature, it is difficult to ensure that the temperature measured is the “true” surface temperature. In most cases, the presence of a thermocouple will perturb the temperature distribution at the attachment point. The temperature measured is the perturbed temperature. Such error is called measurement error which can be expressed as [117]:

$$Z = \frac{T_s - T_i}{T_s - T_a} \quad (3.8)$$

where Z is the installation factor, T_s the true surface temperature, T_i the temperature indicated by the thermocouple and T_a the surrounding temperature. As shown in Table 3.1, the measurement error increases as the surface temperature increases.

A proper installation of thermocouple helps to reduce the measurement error [117]. In this calibration procedure, a high thermal conductive and low heat capacity thermal epoxy is applied to reduce the measurement error. High thermal conductivity epoxy ensures proper contact of the thermocouple to the surface. Low heat capacity minimizes perturbation of the temperature field.

3.3 Materials and devices employed

Polystyrene

Polystyrene sheet with 1.2 mm thickness purchased from Goodfellow was used in this investigation. The grade No. is ST313120 with a molecular weight of 267.8 kg/mol [118]. The glass transition temperature (T_g) is around 100 °C. Thermal conductivity at 23°C ranges from 0.1 to 0.13 W/ (m K). Material density is 1.05 g/cm³. Specific heat capacity is 1200 J/(K kg).

Thermocouple

Type K thermocouple provided by RS is used for temperature measurements. The temperature range of this thermocouple is from -100°C to +250°C. The accuracy of the thermocouple is +/- 1°C. The tip diameter is 0.2 mm.

Thermometer

A four-channel data logging thermometer purchased from General Tool is employed to register the temperature from the thermocouples. The minimum temperature measured is -200 °C and maximum temperature measured is 1370 °C. The resolution is 0.1 °C with accuracy of ± 2 °C. Up to 1600 data points can be stored. The minimum recording rate is 1 Hz. The T_{99} (time taken from initial value to achieve 99% of final value [119]) is around 5 s. The calibration is to be carried out at steady state to avoid any potential error due to thermal inertia.

Thermal bonding epoxy

TBS thermal bonding epoxy purchased from RS is used to bond thermocouples to the sample surface. The thermal conductivity of TBS bonding epoxy is 1.1W/mK. The heat capacity is 0.5 cal/g/°C at 30 °C.

Paint

The PNM400 black paint purchased from RS is employed for painting the surface to increase its emissivity.

3.4 Calibration experiment set-up

3.4.1 Sample preparation

The calibration temperature of PS was from 25°C to 100 °C. Black painted PS was employed for temperature calibration to reduce noise due to emissivity.

The sample preparation procedure was as follows:

1. With a CNC machine (INTERMECH MACHINERY PTE LTD, ISEL CNC drilling/milling machine), three holes of 1 mm diameter and 1 mm depth were drilled on the substrate for thermocouple attachment, namely the TC holes. The sample was subsequently end milled into a rectangular piece of 30 mm x 30 mm.
2. The sample was cleaned with DI water to remove any debris.
3. Three thermocouples were placed on the thermocouple holes and bonded to the sample surface by thermal epoxy.

4. Masked thermocouple attached areas were painted black with PNM 400 black paint. The mask was same size as the sample, and contained three circular openings with the same areas and relative locations as the three drilled holes for thermocouples. The mask facilitated the painting of three black circular locations on the sample surface corresponding to the three thermocouple locations on the opposite surface, see Fig. 3.5.
5. The sample was clamped by an aluminum sample holder after the thermal bonding epoxy was fully cured (48 hours). A black cover was made to reduce thermal noise from the surroundings as shown in Fig. 3.6.

Fig. 3.5 Sample preparation.

3.4.2 Calibration procedures

Fig. 3.6 Calibration set-up.

The calibration set-up is shown in Fig. 3.6. For proper focusing, the infrared camera was placed approximately 38 mm away from the sample surface. For calibration, the temperature of the location measured by the infrared camera had the same corresponding location as a thermocouple on the opposite surface of the sample; this is with the implicit assumption that the temperature at these corresponding locations have the same temperature.

The calibration procedure was as follows:

Step 1. The sample was heated up to 25 °C, and subsequently increased with an interval of 5 °C. Step 2. The temperature of the black painted area was measured by the infrared camera. The thermocouple temperature was recorded.

Step 3. For each measurement (at an interval of 5 °C), the temperatures captured and recorded by thermocouples and infrared camera were monitored over time until they are stable (little fluctuation of temperature). Generally it takes two minutes to become stable. After the temperature became stable, the temperature over two minutes was recorded.

Steps 1 to 3 were repeated until the maximum temperature of 100 °C (glass transition temperature of PS) had been reached.

Three thermocouple and the corresponding infrared camera readings were obtained as depicted in Fig. 3.7 and Table 3.2. There is excellent correlation between thermocouple readings and infrared camera readings, with $R^2 = 0.9993$. The standard error of slope and intercept is 0.0040 and 0.1740 respectively.

Fig. 3.7 Calibration curve for black painted PS.

Table 3.2 Temperature readings of infrared camera and thermocouples at different position.

Temperature captured by infrared camera (°C)			Temperature captured by thermocouples (°C)		
Cam1	Cam2	Cam3	TC1	TC2	TC3
27.98	26.96	29.20	28.85	28.33	29.82
30.36	29.35	28.65	31.40	30.86	29.14
33.37	32.51	35.65	34.32	34.17	36.40
36.59	35.04	38.09	37.58	36.45	39.45
38.99	35.51	38.85	40.05	37.11	40.28
42.40	39.23	42.63	43.24	40.87	43.58
43.70	41.90	46.84	44.34	43.67	47.85
45.07	45.30	52.97	45.86	46.89	54.01
47.54	48.48	53.75	48.37	49.97	54.65
50.62	51.75	58.89	51.49	53.53	60.32
53.24	54.05	62.35	53.73	55.55	63.69
53.74	57.31	64.55	54.20	58.85	66.27
56.02	57.57	67.66	56.55	59.33	69.46
58.67	63.98	71.00	59.24	65.67	72.49
59.91	66.20	75.44	60.40	67.68	76.61
64.41	68.74	78.35	64.34	70.11	80.17

Chapter 4 Femtosecond laser-induced nonlinear absorption

4.1 Introduction

Photon absorption is an important phenomenon as it is the first step of laser-material interaction. During femtosecond laser-material interaction, nonlinear absorption is induced and dominating the absorption process, especially for a material transparent to the laser wavelength.

In this investigation, z scan technique was applied for the determination of nonlinear absorption coefficient. As discussed in chapter 2, most of the previous studies only focused on thin samples. There are only few investigations on thick samples and the investigations were limited to theoretical analysis.

Compared with thin samples, the nonlinear behavior of a thick sample was more complicated. However, in practice, thick samples were much more widely used. Thus, there was a need to investigate the nonlinear absorption behavior of thick samples, both theoretically and experimentally.

4.2 Experiment procedures

The energy absorption at different laser intensity was experimentally measured. The experiment set-up is shown in Fig.4.1.

Fig. 4.1 Experimental set-up for nonlinear absorption coefficient measurement.

A Quantronix integra-C femtosecond laser with pulse duration of 130 fs was employed in this experiment. The laser wavelength is 795 nm. The laser beam with Gaussian distribution was focused through an f- θ lens with a focal length of 163 mm. Defocused beam diameter before the scanner is 7 mm. The focal spot diameter is 30 μm . The beam diameter at different z position can be calculated by:

$$\omega_z^2 = \omega_0^2 (1 + z^2 / z_0^2) \quad (4.1)$$

Where z is the distance from the focal plane to the sample surface, ω_0 the focal spot radius and z_0 the Rayleigh range.

A FieldMaxII power meter with PM30 thermal sensor purchased from Coherent was employed for power measurements. The diameter and maximum power of a beam that can be measured are 30 W and 19 mm respectively. The maximum power density and maximum energy density of the thermal sensor was 6 kW/cm^2 and 600 mJ/cm^2 respectively. The power density I and energy density F of the laser beam can be expressed as:

$$I = \frac{P}{\pi\omega_z^2} \quad (4.2)$$

$$F = \frac{E}{\pi\omega_z^2} \quad (4.3)$$

To avoid damaging the power meter, I and F should not exceed the maximum power density and energy density of the thermal sensor. The maximum power of the femtosecond laser is 1.5 W. Thus, the minimum ω_z should be larger than 0.28 mm; this means that the minimum distance between the power meter and the focal plane is to be 16.69 mm. The diameter of the thermal sensor is 19 mm; to ensure that the whole laser beam is within the thermal sensor, the maximum distance between the sensor and the focal plane should be less than 56.4 cm.

The experiment procedure was as follows:

1. The thermal sensor was placed under the scanner (or lens) and the power meter was connected to the PC. The thermal sensor was connected to the meter and aligned by the leakage of laser. The mechanical shutter and lighting system were turned off during the alignment.
2. The position of scanner was adjusted to be around 30 cm away from the thermal sensor. The focal length of the scanner was 163 mm.
3. The PS sample was clamped with a sample holder and the sample holder was fixed to an X Y Z table. The distance between the sample and the thermal sensor was fixed to be around 15 cm as shown in Fig. 4.2.
4. The scanner position was adjusted for the laser beam to focus on the sample surface.

5. The sample was removed. The laser was turned on and the laser power was adjusted. The value of laser power was recorded over 2 mins.
6. A blank sample was placed on the top of the thermal sensor and the laser power was measured. The transmitted power was the power after sample reflection and linear absorption. This power was then set as the incident power.
7. The clamped sample was put in place and fixed at the focal plane.
8. The laser was turned on and its power reading was recorded over 3 s.
9. The scanner was moved in the negative direction with a step size of 0.5 mm. The laser was moved to a different area on the sample after each measurement. This was to avoid the effect of laser induced properties changes by the previous measurement.
10. Step 9 was repeated in the positive direction.
11. The sample was removed and the value of laser power was recorded for 2 mins (for checking of laser power stability before and after the measurement).
12. Step 5 to step 11 was repeated for different laser power.
13. A curve of transmittance versus sample position z was obtained after the measurements.

Fig. 4.2. Experimental set-up for nonlinear absorption measurements.

4.3 Theoretical analysis

The experimental results may be interpreted with the standard z scan technique [120]. The nonlinear absorption can be generally described as:

$$\frac{dI}{dz'} = (\alpha + \beta I)I \quad (4.4)$$

where I is the laser intensity, α is the linear absorption coefficient and β is the nonlinear absorption coefficient. By solving equation 4.4, the irradiance distribution at the exit surface of a sample can be calculated as [120]:

$$I_e(z, r, t) = \frac{I(z, r, t)e^{-\alpha L}}{1 + q(z, r, t)} \quad (4.5)$$

where $I_e(z, r, t)$ is the laser intensity at the exit surface of the sample. $I(z, r, t)$ is the laser intensity without energy absorption, and [120]

$$q(z, r, t) = \beta I(z, r, t) L_{eff} \quad (4.6)$$

$$L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha} \quad (4.7)$$

Without any nonlinear absorption ($\beta=0$), equation 4.5 becomes [120]:

$$I_e(z, r, t) = I(z, r, t) e^{-\alpha L} \quad (4.8)$$

Equation 4.8 is the standard Beer-Lambert law for linear absorption. As shown in Fig. 4.3, the linear absorption coefficient α is measured to be close to zero by employing a UV-VIS-NIR scanning spectrophotometer (UV-3101PC, SHIMADZU). At 795 ± 10 nm, which is the wavelength of the femtosecond laser employed, the laser beam absorbance was around 0 %, transmission 90.5 % and reflection 9.2 %. This means that the linear absorption of laser beam during femtosecond laser PS interaction is negligible; the dominant absorption mechanism is through nonlinear absorption.

Fig. 4.3 Photon absorption of PS under different wavelength.

With negligible linear absorption ($\alpha=0$), $L_{eff}=L$ and L is the sample thickness; equation 4.5 becomes [120]:

$$I_e(z, r, t) = \frac{I(z, r, t)}{1 + q(z, r, t)} \quad (4.9)$$

The instantaneous transmitted power can be obtained by spatially integrating equation 4.5 [120]:

$$P(z, t) = P_i(t) e^{-\alpha L} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \quad (4.10)$$

$$P_i(t) = \pi \omega_0^2 I_0(t) / 2 \quad (4.11)$$

$$q_0(z, t) = \beta I_0(t) L_{eff} / (1 + z^2 / z_0^2) \quad (4.12)$$

Where $P(z, t)$ is the instantaneous transmitted power and $P_i(t)$ is the instantaneous incident power.

For a temporally Gaussian pulse, equation 4.10 can be time integrated to give the normalized transmittance (i.e transmitted power over incident power) [120]:

$$TR(z) = \frac{1}{\sqrt{\pi} q_0(z, 0)} * \int_{-\infty}^{+\infty} \ln(1 + q_0(z, 0) e^{-\tau^2}) d\tau \quad (4.13)$$

$$TR(z) = \sum_{m=0}^{\infty} \frac{[-q_0(z, 0)]^m}{(m+1)^{3/2}} \quad (4.14)$$

For thin sample (sample thickness less than the Rayleigh range), m is simply equal to 1. For $m=1$, equation 4.14 allows the nonlinear absorption coefficient β be obtained by matching the TR versus Z curve obtained from experiment.

This analysis is only applicable for a sample with thickness less than the laser Rayleigh range z_0 . The Rayleigh range is defined as [120]:

$$z_0 = \frac{\pi \omega_0^2}{\lambda} \quad (4.15)$$

where ω_0 is the focal spot radius (15 μm) and λ is the laser wavelength (795 nm).

For this investigation, the Rayleigh range is calculated to be around 0.889 mm.

The PS sample thickness is 1.2 mm which is larger than the Rayleigh range. Thus, the sample is considered as a thick sample which required a more detailed analysis. Zang and his group [61] have provided an analytic solution to characterize a thick media with nonlinear absorption. For a thin medium, equation 4.10 may be re-written for the instantaneous normalized transmittance TR as [120]:

$$TR(z, t) = \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \quad (4.16)$$

A thick sample may be treated as a stack of many thin samples [61]. The normalized transmittance of a thick sample can be written as a summation of these many layers of thin samples as [61]:

$$\begin{aligned} TR(z, t) = & \prod_{i=1}^n \left\{ \frac{1}{q_{0i}(z_i, t)} \ln[1 + q_{0i}(z_i, t)] \right\} \cong 1 - \frac{1}{2} \sum_{i=1}^n q_{0i}(z, t) + \left[\frac{1}{2} \sum_{i=1}^n q_{0i}(z, t) \right]^2 \\ & + O \left\{ \left[\frac{1}{2} \sum_{i=1}^n q_{0i}(z, t) \right]^3 \right\} \end{aligned} \quad (4.17)$$

To transform the summation to an integral for ease of calculation, equation 4.17 can be approximated as [61]:

$$TR(x, t) = \frac{1}{1 + \frac{1}{2} \sum_{i=1}^n q_{0i}(x, t)} = \frac{1}{1 + \frac{1}{2} \int_x^{x+l} q_0(x, t) dx} \quad (4.18)$$

Where $x = z / z_0$ and $l = L / z_0$. The truncation error from equation 4.17 to 4.18 is second order. With integration of equation 4.18, the normalized transmittance becomes [61]:

$$T = \frac{1}{1 + \frac{1}{2} * Q_R [\tan^{-1}(x+l) - \tan^{-1}(x)]} \quad (4.19)$$

Where $Q_R = \beta I_0 z_0$. I_0 is the peak laser intensity at the irradiation center.

4.4 Results and discussion

The theoretical and experimental normalized transmittances at different laser power of 5.2 mW, 10.4 mW, 14.4 mW and 23.5 mW are shown in Figs. 4.4, 4.5 and 4.6 and 4.7 respectively. Least square fitting the experiment data with equation 4.19, the nonlinear absorption coefficient β was determined to be 0.00066 m/W, 0.00071m/W, 0.00072 m/W and 0.00069 m/W with R^2 values of 0.92, 0.94, 0.95, and 0.91 respectively. The average β was 0.000695 m/W with a standard deviation of 0.000026.

Fig. 4.4 Normalized transmittance z scan curve for 1.2 mm PS sample at a wavelength of 795 nm with laser power at 5.2 mW. The peak laser intensity was $1.13 \times 10^{13} \text{ W/cm}^2$. The black dots are the experiment data while the red line is the fitting curve using equation 4.19.

Fig. 4.5 Normalized transmittance z scan curve for 1.2 mm PS sample at a wavelength of 795 nm with laser power at 10.4 mW. The peak laser intensity was $2.26 \times 10^{13} \text{ W/cm}^2$. The black dots are the experiment data while the red line is the fitting curve using equation 4.19.

Fig. 4.6 Normalized transmittance z scan curve for 1.2 mm PS sample at a wavelength of 795 nm with laser power at 14.4 mW. The peak laser intensity was $3.13 \times 10^{13} \text{ W/cm}^2$. The black dots are the experiment data while the red line is the fitting curve using equation 4.19.

Fig. 4.7 Normalized transmittance z scan curve for 1.2 mm PS sample at a wavelength of 795nm with a laser power at 23.5mW. The peak laser intensity was $5.12 \times 10^{13} \text{ W/cm}^2$. The black dots are the experiment data while the red line is the fitting curve using equation 4.19.

The transmittance increased as the distance between the sample and the focal plane increased either in the positive or negative direction. For instance, the normalized transmittance at $z = 0$ mm was 0.12, while it increased to 0.44 at $z = 1$ mm and 0.5 at $z = -3$ mm as shown in Fig. 4.4. This increase in transmittance was due to the decreased laser intensity. As the sample moved away from the laser focal position, the laser intensity decreased, the absorption decreased, thus the transmittance increased.

The valley shown in Fig. 4.7 for a laser power of 23.5 mW was much wider than that in Fig. 4.4 for a laser power of 5.2 mW. This indicates that for the higher laser intensity at 23.5 mW, even though the sample was further away from the focus plane, the laser intensity was high enough to induce high absorption. Thus the valley became wider at higher laser power.

As the material was thick, the transmittance may vary as the beam travels through the thickness. To facilitate an appreciation of the variation of transmittance as a function of laser intensity, average laser intensity is calculated as [1]:

$$I_{ave} = \frac{P}{A_{ave}} \quad (4.20)$$

Where I_{ave} is the average laser intensity, P is the laser power and A_{ave} is the average laser irradiation area. A_{ave} can be calculated by:

$$A_{ave} = \frac{V_{irr}}{H} \quad (4.21)$$

Where V_{irr} is the laser irradiation volume as shown in Fig. 4.9 and H is the sample thickness which is 1.2 mm. To calculate the V_{irr} , three scenarios are to be considered: laser focused above the sample, within the sample and below the sample as shown in Fig. 4.8.

Fig.4.8 Section view of sample when laser was focused a) above the sample, b) within the sample and c) below the sample.

For laser focused above and below the sample, the V_{irr} can be calculated as the volume of a circular truncated cone. For laser focused within the sample, V_{irr} can be calculated by adding the two circular truncated cone volumes within the sample. The volume of a circular truncated cone can be calculated as [121]:

$$V = \frac{1}{3}\pi(r_1^2 + r_1r_2 + r_2^2)h \quad (4.22)$$

where r_1 and r_2 are the top and bottom surface radius, h is the height.

The relationship between this average laser intensity at four different incident powers (5.2 mW, 10.4 mW, 14.4 mW and 23.5mW) and the normalized

transmittance was shown in Fig. 4.9. As depicted in Fig. 4.9, the normalized transmittance decreased (absorption increased) as the intensity increased.

Fig.4.9 The normalized transmittance at different laser intensity.

4.5 Summary

In this chapter, the nonlinear absorption behavior of thick PS sample was theoretically analyzed and experimentally investigated. Z scan technique was applied for the analysis. The thick sample was treated as a stack of thin samples and the nonlinear absorption coefficient of PS was determined to be 0.000695 m/W with a standard deviation of 0.000026. The nonlinear behavior at different powers, namely 5.2 mW, 10.4 mW, 14.4 mW and 23.5 mW were investigated. As the laser intensity increased, the absorption increased while the transmittance decreased. This is consistent with the theoretical analysis.

Chapter 5 Thermal effects of fs laser--polystyrene interaction

5.1 Introduction

In chapter 4, nonlinear energy absorption has been introduced and discussed. Subsequent to energy absorption, the energy is dissipated into the bulk material as heat. Heat conduction and thermal effect are important as they have effects on the machining precision and material property after laser treatment. The thermal effect of ultrashort pulsed laser is significantly less as compared to long pulsed laser and continuous laser. However, as demonstrated by Lam and his group [35-37] on the interaction of femtosecond laser with opaque materials, there is still a large percentage of laser energy that is converted to heat energy.

In contrast to the previous investigations of Lam's group [35-37] on non-transparent materials, this investigation focuses on femtosecond laser interaction with PS, which is transparent to the laser beam employed. Heat dissipation (subsequent to nonlinear energy absorption) will be investigated experimentally and correlated with simulations.

5.2 Experiment procedures

By employing an infrared camera, the temperature profile of a sample can be directly observed. The experiment set-up for temperature measurements is shown in Fig. 5.1. The symbol z is defined as the relative distance between the sample top surface and the laser focal position. A series of experiments at different laser powers and different z positions were conducted.

Fig. 5.1 Experimental set-up for temperature measurement of femtosecond laser PS interaction. $z=0\text{mm}$ when laser focus on the top sample surface.

As shown in Fig. 5.1, the PS sample ($1.2\text{ mm} \times 1.2\text{ mm} \times 30\text{ mm}$) was placed horizontally. Laser irradiation was focused along the centerline of the sample. The temperature changes as a function of time at different z positions were measured from one vertical (side) surface of the sample with an infrared camera. This vertical surface was painted black to increase its emissivity. Power meter was placed under the sample to monitor the power changes in the far field during the process.

The experimental procedure was as follows:

1. PS sample with dimensions of $30\text{ mm} \times 1.2\text{ mm} \times 1.2\text{ mm}$ (length $\times$ width $\times$ thickness) was machined using a CNC machine (INTERMECH MACHINERY PTE LTD, ISEL CNC drilling/milling machine).
2. The sample was painted black on both front and back vertical surfaces using PNM 400 black paint (emissivity of 0.993). The sample was held vertically by a sample holder.

3. Femtosecond laser beam was focused on the middle of the sample. FLIR SC5000 thermal camera was focused perpendicularly on the sample vertical surface for recording sample temperature during laser processing as shown in Fig. 5.1.
4. The power of femtosecond laser was measured by a power meter for the whole process, i.e. before, during and after the experiment.
5. Once the laser was turned on, the camera was triggered to commence recording the temperature profile of the sample.
6. The laser power was turned off after 20 seconds. A curve of temperature changes versus time was obtained.
7. Repeat steps 1 to 6 for laser focused at different positions of the sample. Laser was focused below the bottom surface of the sample, within the sample and above the top surface of the sample.

5.3 Results and discussion

The temperature changes at different z positions were investigated. The incident power was measured to be 5.7 mW. The sample temperature profiles at different time (1s, 5s and 10s) are shown in Fig. 5.2.

As presented in Fig. 5.2, the sample temperature increased with the irradiation time for z varied from -3 mm to 3 mm. For instance, at $z = 0$ mm, the temperature was higher at 10 s than 5 s. In contrast, there was almost no temperature changes over time at $z = -4$ mm and $z = 4$ mm, indicating negligible absorption of laser power by the sample. This is due to the highly decreased laser intensity when the sample was placed far away from the focal position. The temperature increased more as the

sample was placed nearer to the focal position. For instance, the temperature was higher at $z = 2$ mm than $z = 3$ mm for the same time instant. This was due to the increased absorption with higher laser intensity.

Fig. 5.2 Sample temperature profiles (in Celsius) at different time with z varied from -4 mm to 4 mm.

The temperatures at different positions of the sample were further analyzed, see Fig. 5.3. Four positions were chosen for the analysis: positions A (0.4 mm left of laser irradiation center), B (laser irradiation center), C (0.4 mm right of laser irradiation center) and D (0.4 mm in laser propagation direction from irradiation center). The results are shown in Fig. 5.4.

Fig. 5.3 Locations of sample temperature measured.

As shown in Fig. 5.4, at $z = 0$, the maximum temperature at position B was around 39°C . The temperature changes at position A and position C were almost the same. At $z = 1\text{ mm}$, $z = -1\text{ mm}$ and $z = -2\text{ mm}$, the maximum temperature at position B was around 40°C . This is because when laser was focused at a short distance away from the sample surface, the irradiation area increased and the laser intensity decreased; as such, the absorption efficiency decreased as the absorption coefficient decreased with a decrease in laser intensity. The energy absorbed and was subsequently conducted into the material as heat, raising its temperature. When the laser was focused further away from the sample, the irradiation area was further increased

with associated decreased in laser intensity. When the laser intensity decreased sufficiently, there will be much less absorption. For instance, at $z = -3$ mm and $z = 3$ mm, the maximum sample temperature was only around 31°C and 30°C respectively. When $z = -4$ mm and $z = 4$ mm, there was almost no absorption and negligible temperature changes could be detected.

Fig. 5.4 Temperature measured at different positions: A, B, C and D as shown in Fig. 5.4 at different z positions (unit in mm) at a power of 5.7 mW.

The temperature changes at a laser power of 8.47 mW at different z positions were also investigated as presented in Fig. 5.6 with z varied from -6 mm to 6 mm. As presented in Fig. 5.5, the temperature increased more as the sample position is near to the focal position. At $z = -6$ mm and $z = 6$ mm there is almost no temperature changes over time, indicating negligible absorption of laser power by the sample. For sample positions A, B, C and D as shown in Fig. 5.3, the temperatures at different z positions were measured and shown in Fig.5.6.

Fig.5.6 indicates that the maximum temperature at position B was around 40°C when the laser was focused on the sample surface. The maximum temperatures at position B of the sample was around 45°C and 41°C at $z = -2$ mm and $z = 2$ mm respectively. These temperatures were higher than the laser focused on the sample surface at $z = 0$. This may due to several reasons:

When the laser was focused on the sample surface, the laser intensity at the irradiation center (position B) was sufficient high to cause material removal and material property changes (this phenomenon will be discussed in chapter 6). Thus, part of the laser energy would be consumed for material removal and property changes. In contrast, when laser focused far away from the sample, the irradiation area increased and the laser intensity decreased; as such, even the absorption efficiency decreased, most of the energy was absorbed and later conducted away as heat. Under this circumstance, much less energy was consumed for material removal and property changes.

Fig. 5.5 Temperature profiles of sample at different time with z varied from -6 mm to 6 mm. The temperature unit is in Celsius.

Fig. 5.6 Temperature measured at different position: A, B, C and D as shown in Fig.

5.3 at different z positions (unit in mm) at a power of 8.47 mW.

5.4 Summary

The laser induced temperature changes at different laser power during laser-material interaction were experimentally investigated. It was observed that the temperature increased more when the sample was placed near to the focal position. When the laser beam was focused at a short distance from the sample surface, the irradiation area increased and the laser intensity decreased, with a corresponding decrease in the absorption efficiency coefficient. The absorbed energy was subsequently conducted away as heat resulting in a temperature increase of the sample. When the laser was focused further away from the sample, the irradiation area was further increased with further associated decreased laser intensity. When the laser intensity decreased sufficiently, there will be negligible absorption as almost all the laser power will be transmitted through the sample.

Chapter 6 Simulation of thermal effects

6.1 introduction

In chapter 4, femtosecond laser induced nonlinear absorption has been discussed. After the energy has been absorbed, the energy will be dissipated into the bulk material as heat. In chapter 5, heat conduction and thermal effects have been experimentally studied, indicating that the temperature can increase significantly during the laser-material interaction process. This indicates a large percentage of laser energy can be converted to heat energy and dissipated into the bulk material. In this chapter, heat conduction simulation was conducted and compared with the experimental results.

6.2 Methodology

A 3D finite element (FE) model of 0.6 mm x 1.2 mm x 15 mm was developed to simulate the evolution of temperature profile during femtosecond laser PS interaction. The commercial finite element (FE) software "COMSOL Multiphysics" was employed.

Governing equation:

The FE simulation of heat conduction assumes that the absorbed laser energy can be modelled as a heating source; the process is governed by the time dependent heat diffusion equation:

$$\rho C_p \frac{\partial T}{\partial t} + \nabla \cdot (-k \nabla T) = Q \quad (6.1)$$

Where ρ is the material density, C_p is the heat capacity, k is the thermal conductivity and Q is the laser energy absorbed by the material and later converted to heat energy.

Boundary conditions

The absorbed energy from an incident laser beam is treated as an input heat source to simulate the heat conduction within a sample. As discussed in the nonlinear absorption section in chapter 4, for a thin film the transmitted laser intensity from a sample after absorption is [120]:

$$I_e(z, r, t) = \frac{I(z, r, t)e^{-\alpha L}}{1 + q(z, r, t)} \quad (4.5)$$

where $I_e(z, r, t)$ is the transmitted laser intensity at the exit surface of the sample.

$I(z, r, t)$ is the laser intensity without energy absorption.

With negligible linear absorption, integration equation 4.5 over r , the normalized transmittance for a thin sample becomes [61]:

$$TR = \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \quad (4.16)$$

As discussed in chapter 4, section 4.3, the sample thickness is 1.2 mm which is larger than the Raleigh range (0.889mm). Thus, the sample is considered as a thick sample. A thick sample may be treated as a stack of thin layers. The output transmittance from the sample becomes the product of the transmittance of all layers as [61]:

$$TR = \prod_{i=1}^n \left(\frac{\ln[1 + q_{0i}(z_i, t)]}{q_{0i}(z_i, t)} \right) \quad (4.17)$$

For example, if the transmittance of layer 1 and layer 2 is 0.5 and 0.7 respectively, the overall transmittance after layer 2 is $0.5 \times 0.7 = 0.35$. To simplify the process,

the sample is divided into six layers with each layer having a thickness of 200 μm as shown in Fig. 6.1. The laser beam was assumed to maintain its Gaussian distribution during the process. Indeed, the analytical solution of a thick sample (discussed in chapter 4) also assumes that the laser beam maintains its Gaussian distribution.

Fig. 6.2 shows the transmittance of the analytical solution (using equation 4.19 in chapter 4) and the six-layer model. The incident laser power was set according to the experiment values. The nonlinear absorption coefficient β was set to be 0.000695 m/W according to the values obtained from chapter 4. It can be shown subsequently that the maximum error between the analytical solution and the six layer model was calculated to be less than 3.3%.

Fig. 6.1 The sample is divided into six layers with a layer thickness of 200 μm .

The laser intensity inside different layer denoted by I_i (i is the layer number), transmitted laser intensity from different layer denoted by I_{out_i} and laser

transmittance of different layer denoted by TR_i can be calculated by the following equations:

$$i=1 \left\{ \begin{aligned} I_1(z, r) &= I_{out}(z_{out}, r, \beta = 0) \frac{\ln(1 + \beta I_{in-p} z')}{\beta I_{in-p} z'} \quad (6.2) \\ I_{out-1}(z, r) &= I_{out}(z_{out}, r, \beta = 0) \frac{\ln(1 + \beta I_{in-p} * 0.0002)}{\beta I_{in-p} * 0.0002} \quad (6.3) \\ TR_1 &= \frac{\ln(1 + \beta I_{in-p} * 0.0002)}{\beta I_{in-p} * 0.0002} \quad (6.4) \end{aligned} \right.$$

$$i>1 \left\{ \begin{aligned} I_i(z, r) &= I_{out}(z_{out}, r, \beta = 0) * \prod_{i=1}^{i-1} TR_i * \frac{\ln(1 + \beta I_{out-i-1-p} z')}{\beta I_{out-i-1-p} z'} \quad (6.5) \\ I_{out-i}(z, r) &= I_{out}(z_{out}, r, \beta = 0) * \prod_{i=1}^{i-1} TR_i \quad (6.6) \\ TR_i &= \frac{\ln(1 + \beta I_{out-i-1-p} * 0.0002)}{\beta I_{out-i-1-p} * 0.0002} \quad (6.7) \end{aligned} \right.$$

Where $I_{out}(z_{out}, r, \beta = 0)$ is the laser intensity without linear and nonlinear absorption. It can be described as [120]:

$$I_{out}(z_{out}, r, \beta = 0) = I_0 e^{\frac{-2r^2}{w_0^2}} \frac{1}{(1 + (z/z_0)^2)} \quad (6.8)$$

Where I_0 is the peak laser intensity at the focus plane, r is the distance from the irradiation center, z is the distance from the focal plane. I_{in} is the incident laser

intensity. I_{in_p} is the peak incident laser intensity. $I_{out\_i\_p}$ is the transmitted peak laser intensity from layer i . z' is the distance from the layer surface.

Fig. 6.2 Comparison of the normalized transmittance of the analytical solution by using equation 4.19 in chapter 4 and the six layers model.

The laser intensity distribution along the laser propagation direction within the sample when the laser was focused at different position for different nonlinear absorption coefficient was also investigated as shown in Fig. 6.3.

a) Focus on the sample surface.

b) Focus in mid-section within the sample
(0.6 mm from the sample surface).

c) Focus on the bottom of the sample (1.2 mm from the sample surface).

Fig.6.3 Laser intensity distribution within sample along laser propagation direction when laser focused a) on top surface of sample, b) in mid-section within the sample and c) on bottom surface of sample with different assumed absorption coefficient.

The absorbed laser energy dI/dz was treated as a heat source. For instance, βI_1^2 is the heat source for layer 1 and βI_2^2 is the heat source for layer 2. Since the laser irradiation is at the centerline of the sample, it is symmetric along the x-z and y-z plane. As such, only a quarter of the sample was simulated without compromising

accuracy. Fig. 6.4 presents a 3D view of the FE model. The boundary conditions are shown in Fig.6.5 and Table 6.1.

Fig. 6.4 3D view showing quarter FE model.

Fig. 6.5 Boundary surfaces for FEM simulation.

Table 6.1 Boundary conditions for FEM simulation

Boundary conditions	Symmetric surface	Constant temperature	Heat source input	surface-ambient irradiation	Natural convection by air
Boundary surfaces	5, 4	6	All layers (different heat source input for different layer)	1, 2, 3	1, 2, 3

Heat exchanges with the environment during the process are described by the appropriate boundary conditions. Heat is dissipated through the surface by ambient radiation:

$$-k\nabla T = \varepsilon\sigma(T_{amb}^4 - T^4) \quad (6.9)$$

and natural convection between the material and air:

$$-k\nabla T = h(T_{amb} - T) \quad (6.10)$$

where T_{amb} is the ambient temperature, ε is the emissivity of material, which is set to be 0.993 (the emissivity of black paint used in the experiments). σ is the Stefan's constant equals to $5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4}$, T is the material temperature, h is the air convection coefficient which can be calculated as [122]:

$$h = \frac{k \cdot \overline{Nu}_L}{L} \quad (6.11)$$

$$\overline{Nu}_L = 0.68 + \frac{0.670 Ra_L^{1/4}}{\left[1 + \left(\frac{0.492}{Pr} \right)^{9/16} \right]^{4/9}} \quad (6.12)$$

where $\overline{Nu}_L$ is the Nusselt number, Ra_L and Pr are the Rayleigh and Prandtl dimensionless numbers. Nusselt number is defined as the ratio of heat convection and conduction across the boundary. Rayleigh number describes the relationship between buoyancy and viscosity which is given by:

$$Ra_L = Gr_L * Pr \quad (6.13)$$

Gr_L is Grashof dimensionless number defined as:

$$Gr_L = \frac{g\beta(T - T_\infty)L^3}{\nu^2} \quad (6.14)$$

where $g = 9.81 \text{ m/s}^2$ is the gravitational acceleration. $\beta = 0.00343/\text{K}$ is the thermal expansion coefficient for air at 20°C . T is the sample surface temperature and T_∞ is

the temperature at infinity which is equal to the ambient temperature (21°C). L is characteristic length; for a rectangular cross-section it is equal to the area divided by the circumference. [123]. ν is the kinematic viscosity with a value of $15.06 \times 10^{-6} \text{ m}^2/\text{s}$ at 20°C [124].

Prandtl number is given by the ratio of momentum diffusivity and thermal diffusivity:

$$\text{Pr} = \frac{c_p \mu}{k} \quad (6.15)$$

where $C_p = 1005 \text{ J}/(\text{kg} \cdot \text{K})$ is the heat capacity of air at 20°C [124], μ is the dynamic viscosity with a value of $1.816 \times 10^{-5} \text{ kg}/(\text{m} \cdot \text{s})$ at 20°C [124] and k is the thermal conductivity with a value of $0.02561 \text{ W}/(\text{m} \cdot \text{K})$ at 20°C [124].

For the simulations (and during experiments), the temperature increased significantly on surfaces 1, 2 and 3. The temperature of the side surface (surface 6) does not changed much as it is far away from the irradiation center. The heat exchanges are mainly through surfaces 1, 2 and 3. Thus these surfaces were set to be under natural convection and surface-ambient radiation. The side surface 6 which is far away from the irradiation center were set to be under constant room temperature (293.15K) as shown in Table 6.1.

Meshing

As shown in Fig. 6.6, triangular prism elements were used in the simulations. There were 11,155 mesh elements in total. Extra fine mesh was applied to the volume at the vicinity of the irradiation point. The maximum element size at the irradiation

center was set to be 1 μm . Time step and duration of each simulation are 1 s and 20 s respectively.

Fig. 6.6 FE simulation mesh.

6.3 Results and discussions

Fig. 6.7 shows both simulated and measured temperature profiles at a time of 10 s at laser power of 8.47 mW with $z = 2$ mm. The temperatures at different sample positions were analyzed, see Fig. 6.7 a). Three positions were chosen for the analysis: positions A (laser irradiation center), B (0.4 mm in laser propagation direction from irradiation center) and C (0.4 mm on the right of laser irradiation center). The results are shown in Fig. 6.8, 6.9 and 6.10.

a) Simulated temperature profile (in Celsius) at 10s.

b) Thermal image (in Celsius) captured by infrared camera at 10s.

Fig. 6.7 Typical a) simulated temperature image and b) thermal image captured by infrared camera. Locations of sample temperature measured are shown in Fig. 6.7 a).

Fig. 6.8, 6.9 and 6.10 show the comparisons between simulated temperatures with experimentally measured temperatures at different locations: A, B and C (see Fig. 6.7a)) at different z positions.

Fig. 6.8 Comparison of the simulated temperatures (red line), best fitting curve (dotted blue line, with 50% of incident laser power) with R^2 of 0.95 and experiment measured temperatures (black dots) at $z = 0$ mm.

Fig. 6.9 Comparison of the simulated temperatures (red line), best fitting curve (dotted blue line with 51.9% of incident laser power) with R^2 of 0.92 and experiment measured temperatures (black dots) at $z = 2$ mm.

Fig. 6.10 Comparison of simulated temperatures (red line), best fitting curve (dotted blue line with 26.7% of incident laser power) with R^2 of 0.92 and experiment measured temperatures (black dots) at $z = 4$ mm.

As shown in Fig. 6.8, at $z = 0$ mm, the simulated temperatures were much higher than the experimentally measured temperatures. The error between the simulated results and experimentally measured results was around 21.5%. Much better

agreements were obtained between the simulated and experimental measured results at $z = 2$ mm and $z = 4$ mm. As shown in Fig. 6.9 and Fig. 6.10, the differences between simulated and experimentally measured results were within 2%.

To have an estimation of the laser energy absorbed for heat conduction, the input energy in the simulation was lowered such that the simulated temperature agrees well with the observed temperature; Least square method was applied at all three positions A, B and C simultaneously, see the best fitting curves (dotted blue lines) shown in Fig.6.8 to 6.10. This is summarized in Table 6.2. It was discovered that at $z = 0$ mm, around 50.0% instead of the originally 86.7% (simulated absorbed energy) of the incident laser power was transferred to the bulk material as heat. While at $z = 2$ mm and $z = 4$ mm, 51.9% and 26.7% respectively instead of the originally assumed 52.8% and 27.2% respectively (simulated absorbed energy) was transferred to the bulk material as heat. This means that at $z = 0$, there was a significant difference between the original assumed laser energy absorbed as compared to energy transferred to the material as heat as calculated from its temperature profile; in contract, at $z = 2$ mm and $z = 4$ mm, the agreement between the actual laser power absorbed agreed well with the heat transferred to the material as obtained from its temperature profile.

There are various possible reasons for the rather high difference between simulated laser energy absorbed and experimental heat transferred to the material at $z = 0$ mm. Without any correction, a major assumption of the temperature simulation profile was that all the absorbed energy was used for heat conduction. In this case, the laser incident power was 8.47mW. When the laser was focused on the sample surface, i.e. $z = 0$ mm, the laser intensity at the irritation center was rather high. Indeed, it was

high enough to cause material ablation as shown in Fig. 6.11(a). Since the simulation did not consider material ablation and the associated energy induced by the laser, the assumed energy for heat conduction, and thus the temperature, will be over-estimated, i.e. higher than what it should be.

Fig. 6.11 Cross section view of sample at different z positions at a laser power of 8.47 mW with irradiation time of 20s.

Femtosecond laser induced material ablation is a complicated process, and plasma plump may be generated on the surface during the process [125-129]. Part of the energy for material ablation could well be for plasma generation (material ionization). In addition, the generated plasma could block the interaction between material and laser beam [130, 131], i.e. the plasma shielding effect [132-136].

According to [129], the effects of generated debris and plasma were significant, which could be as high as 40% on the hole drilling efficiency. Although the process was quite complicated, the net result was that less laser energy will be absorbed by and later transferred to the material as heat, and thus conduction and temperature increase. As such, the simulation will overestimate the experimentally observed temperatures.

To have a better appreciation of the relative dominance of laser energy spent in material ablation (including the formation of plasma), shielding by plasma plume, and their effect on energy reduction transmitted to the material as heat, the energy consumed for material ablation can be estimated by considering the associated vaporization and ionization energy required.

The vaporization energy consists of two components: energy consumed for the material to vaporize and the energy for heating up the material to the vaporization temperature. It can be calculated as:

$$E_{vap} = H_{vap} * V * \rho + Cp * V * \rho * \Delta T \quad (6.16)$$

Where H_{vap} is the energy consumed for the material to burn out, which is around 1000 J/g based on the differential scanning calorimetry (DSC) method [137]. For this investigation, V is the ablated material volume, ρ the material density, Cp the material specific heat capacity and ΔT the temperature difference.

The ionization energy was calculated based on the element ionization energy [138, 139]. The molecular expression of polystyrene is $(C_8H_8)_n$ with a mer molecular weight of 104 g/mol [140]. With only two elements, namely hydrogen and carbon, the ionization energy may be calculated by:

$$E_{ion} = M_H ION_H + M_C ION_C \quad (6.17)$$

Where M_H is the mole of hydrogen atom, ION_H the ionization energy of hydrogen atom in kJ/mole, M_C the mole of carbon atom, ION_C the ionization energy of carbon atom in kJ/mole. All the ablated material was assumed to be ionized to plasma. For hydrogen, the first molar ionization energy (1312 kJ/mol) was considered, and for carbon the 3rd molar ionization energy (4620.5 kJ/mol). The calculated energy distributions at various z positions are shown in Table 6.2. The detailed energy calculation was contained in the Appendix A.

Table 6.2 Energy usage distribution (% of incident energy)

(Note: values in columns 3, 4, 5 and 6 sum to value in column 2)

1	2	3	4	5	6
z (mm)	Simulated absorbed energy (without correction)	Energy for heat conduction	Energy used for material vaporization	Energy used for plasma generation (ionization energy)	Effect of plasma shielding & others.
0	86.7%	50.0%	0.1%	34.9%	1.7%
2	52.8%	51.9%	0.1%	-	0.8%
4	27.2%	26.7%	-	-	0.5%

As depicted in Table 6.2, even with ablation, the energy consumed for material vaporization was relatively a minute amount. If the laser intensity was sufficiently high, as shown in Table 6.2, an energy balance calculation indicates that a significant amount of energy would be used for plasma generation, for example at $z = 0$ mm (average laser intensity of 1.2×10^7 W/m²). At $z = 2$ mm, the average laser

intensity of $2.0 \times 10^6 \text{ W/m}^2$ is significantly less than that at $z = 0 \text{ mm}$. Although there was some material ablation, the energy was mainly used for heat conduction, indicating that plasma formation is minimum. This agrees with the understanding that plasma is only formed at high laser intensity. When the laser was defocused further away from the sample surface at $z = 4 \text{ mm}$, the laser intensity was significantly low, with an average laser intensity of $5.6 \times 10^5 \text{ W/m}^2$. No ablation was observed, and almost all of the energy was absorbed by the material, and later converted to heat. These experiments also indicated that for the conditions investigated, plasma shielding and other effects were also small or negligible. This may be due to the short existing time of plasma in ns scale [141-144].

6.4 Summary

The temperature changes for laser PS interactions were simulated and compared with the experimental results. The sample was divided into six thin layers. The results show that when the laser was focused at the sample surface ($z = 0 \text{ mm}$), the simulated temperature was higher than the experimentally measured results. Much better agreements were obtained between the simulated and experimentally measured results at $z = 2 \text{ mm}$ and $z = 4 \text{ mm}$. This was due to laser induced ablation at the surface at high laser intensity. Simple estimates indicate that only a small amount of energy was used for material vaporization during ablation. Plasma generation during ablation is deduced to consume a significant amount of energy, and is the dominant factor in reducing the incident energy reaching the material and subsequently conducted away as heat energy. The energy of plasma generation was

estimated to be around 34.9% of the incident laser energy at $z = 0$ mm when the laser energy intensity is high. Plasma shielding and other effects are around 1.7 % at $z = 0$ mm. At $z = 2$ mm the laser intensity drops to 2.0×10^6 W/m². Although there was some material ablation, the energy was mainly used for heat conduction, indicating that plasma formation is minimum. At $z = 4$ mm, the laser intensity was significantly low (average laser intensity of 5.6×10^5 W/m²). No or negligible ablation was observed, and almost all the laser energy was absorbed and later converted as heat energy within the material.

Chapter 7 Femtosecond laser-induced surface wettability modification

7.1 Introduction

In chapters 4, 5 and 6, the mechanism of laser polymer interaction was investigated. Polymer surface wettability as an application of laser polymer processing will be discussed. As mentioned in chapter 2, wettability is one of the most important surface properties. The controlled surface wettability modification of polymers is desirable and has various applications. For instance, a superhydrophobic surfaces are well suited for self-cleaning of contaminations. A highly hydrophilic surface can improve the surface adhesion and wettability which is desirable for coating and joining applications. Previous study indicates that the surface roughness and surface chemistry have effects on the surface water contact angle (WCA). Some investigations demonstrate that the surface roughness was the dominant factor on surface wettability [38, 44, 103], and others indicate that the surface chemistry dominated wettability [6, 45, 106].

Polystyrene (PS) is a widely used thermoplastic polymer in microfluidic and biological devices. It is transparent and rigid [45], with good resistance to alcohols, concentrated acid, alkaline and polar solvent [107]. The controlled surface wettability modification of PS is desirable as it has various potential applications. These include flow control in microfluidic devices as flow will be retarded by a hydrophobic surface and enhanced by a hydrophilic surface. The pristine static water contact angle (WCA) of PS is measured to be around 88.2°.

Hitherto, there is a lack of understanding of surface modification of polymers by laser irradiation, including the effects of laser power absorption by a polymer on its surface properties. In addition, there are only a few investigations on laser-induced surface modification of PS [1,4], with the modified surface WCA limited to a small range of only 30° [44]. This investigation, therefore, focuses on the laser-induced surface wettability modification of PS. It will attempt to relate the nonlinear absorption of laser power and the associated heating effect on surface properties, and to achieve a wide range of WCA through femtosecond laser induced surface wettability modification of polystyrene.

7.2 Experiment set-up

The experiment set-up is shown in Fig. 7.1. A Ti:Sapphire based fs laser (Quantronix integra-C, USA) was employed to conduct the experiments. A 3 mm x 3 mm surface area was scanned with a scanning speed of 4 mm/s at a fixed hatching density of 0.02 mm. The sample surface was treated at different z position values, where z was defined as the distance between the sample surface and the laser focal position. The surface properties after laser treatment were analyzed using scanning electron microscopy (SEM) (5600LV, Jeol Asia Pte Ltd., Tokyo, Japan), optical profilometer (Alicona, USA) and X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific, UK). The water contact angle (WCA) was measured by applying a sessile drop method. A VCA Optima (VCA-2500XE AST Products, Inc. USA) was employed to measure the surface WCA with a fixed water droplet size of 1 µl. The experiments were conducted in an ambient air environment with a room temperature of 21°C and relative humidity of 60%.

Fig. 7.1 Experiment set-up for laser modification of WCA.

7.3 WCA at different laser intensity

The WCA of virgin PS sample without any laser treatment was measured to be 88.2°. Subsequently, the PS samples were irradiated at different laser intensities (z positions) with a fixed laser power of 10.16 mW. The sample surface laser intensities for various z positions are indicated in Table 7.1.

The surface water contact angles obtained for various z positions were shown in Fig. 7.2. When z was near to 0, the laser intensity was high with high absorption of laser power. The surface WCA angle was increased and the surface became more hydrophobic. For instance, when $z = -2$ mm, $z = -1$ mm, $z = 0$ mm and $z = 1$ mm, the water contact angle was around 145°. The laser intensity decreased with low absorption of laser power when the sample moved further away from the focal position at $z = -4$ mm and $z = 2$ mm, resulting in WCA decreased slightly to around

73° and 80° respectively, which are somewhat hydrophilic. The laser intensity further decreased with negligible laser power absorption at $z = -6$ mm and $z = 3$ mm, resulting in WCA of 87.1° and 87.7° respectively. Indeed, these WCA values are closed to its original water contact angle value of 88.2°, indicating that laser irradiation at these conditions had little effect on the surface properties.

Fig. 7.2 Surface wettability at different laser intensities and z positions at a laser power of 10.16 mW. The pristine WCA is indicated by the star in the figure.

Table 7.1. WCA at different z positions and laser intensity at a power of 10.16 mW.

z positions (mm)	Water contact angle (°)	Laser intensity at surface (W/m ²)	Equivalent peak laser intensity at surface (W/m ²)
-6	87.1	3.09E+05	1.19E+15
-5	79.4	4.41E+05	1.70E+15
-4	73.2	6.77E+05	2.60E+15
-3	148.2	1.16E+06	4.46E+15
-2	146.3	2.37E+06	9.12E+15
-1	144.7	6.35E+06	2.44E+16
0	144.5	1.44E+07	5.54E+16
1	148.0	6.35E+06	2.44E+16
2	80.8	2.37E+06	9.12E+15
3	87.7	1.16E+06	4.46E+15

As discussed in the literature review, the changes of surface wettability may be attributed to a change in surface structure, or surface chemistry, or both. Thus the effects of surface structure and surface chemistry have to be investigated.

The sample surface structure at different z positions at a fixed laser power of 10.16 mW were shown in Fig. 7.3. As shown in Fig. 7.3, the surface was relatively very rough at $z = 0$ mm and $z = 1$ mm. While at $z = 2$ mm the surface became much smoother. There was almost no difference between $z = 2$ mm and the original sample surface. This was because at $z = 0$ mm and $z = 1$ mm, the laser intensity was high with strong laser power absorption resulting in surface structure modification. At $z = 2$ mm, the laser intensity reduced significantly with little laser power absorption. The surface structure remained almost the same.

Fig. 7.3 SEM images of sample surface at different z positions at a laser power of 10.16 mW.

The effect of surface roughness on surface water contact angle was investigated as shown in Fig. 7.4. Pristine surface roughness (R_a) was measured to be around 7.98 nm. As depicted in Fig.7.4, the surface water contact angle increased as the surface roughness increased. This effect was especially pronounced when the surface became very rough, for instance larger than 1.75 μm , the surface became hydrophobic. When the surface was smoother (R_a at 0.08 μm), the surface became a little bit more hydrophilic with a surface water contact angle of around 78° .

Fig. 7.4 Effect of surface roughness on water contact angle. The pristine surface roughness is indicated by the star in the figure.

Surface chemistry is another factor that may have an effect on surface wettability. X-ray photoelectron spectroscopy (XPS) analysis of chemical bonds was conducted by using ESCALAB 250 Xi. The polar groups formed on the surface such as O-C=O, C-O and C=O are believed to be responsible for the change of surface hydrophilicity [104]. Fig. 7.5 shows the C1s spectra of pristine and laser treated samples at $z = 0$ mm and $z = 2$ mm at a power of 10.16 mW. The main peak C-H or C-C bond was at around 285.0 eV. The sub-peaks C-O bond and C=O bond were at 286.3 ± 0.3 eV and 288.3 ± 0.3 eV respectively [86]. The detailed bond information was shown in Table 7.2.

Fig. 7.5 XPS spectra of (a) pristine PS surface and (b) laser treated PS surface at $z = 0$ mm and (c) laser treated PS surface at $z = 2$ mm.

Table 7.2. Polar and non-polar groups formed on PS at different z positions at a power of 10.16 mW.

z positions (mm)	Non- polar groups C- C/C-H (at. %)	Polar group C-O (at. %)	Polar group C=O (at. %)	Sum of polar groups (at. %)	Water contact angle (°)
Pristine	100	-	-	-	88.2
-5	94.16	5.84	-	5.84	79.4
-4	91.28	8.72	-	8.72	73.2
-3	78.38	19.12	2.51	21.63	148.2
-2	78.41	19.1	2.49	21.59	146.3
-1	77.81	18.95	3.23	22.18	144.7
0	78.81	16.58	4.61	21.19	144.5
1	80.24	15.89	3.87	19.76	148.0
2	91.88	7.78	0.34	8.12	80.8
3	92.05	7.01	0.94	7.95	87.7

As presented in Fig. 7.5 and Table 7.2, the oxygen content (polar groups) increased after laser treatment. The total polar groups (at. %) varied with the z positions; this may be due to the varied laser intensity and laser power absorption at different z positions.

At $z = 0$ mm, the laser intensity was high (1.44×10^7 W/m²) and thus high absorption. This may induce a strong reaction between the material surface and ambient air. Thus the sum of the polar groups had a high value of 21.19 (at. %); a higher value of polar group generally will result in a lower water contact angle. However, the measured WCA was high at around 144.5°, indicating a highly hydrophobic condition. This implies that for these experimental conditions, the effect of the polar groups was not the dominating factor for surface wettability. Indeed, the surface roughness was measured to have a value of 2.0 µm. The rougher

surface textures enabled more air trap between the liquid and the surface, which contributed to the hydrophobic condition. For a rough surface, the surface roughness or the surface topography structure played a more significant role in the changes of the surface WCA.

At $z = -4$ mm, $z = -5$ mm and $z = 2$ mm, the surface became somewhat more hydrophilic than that of the pristine sample. At these positions the surface is relatively much smoother and the oxygen content increased. The increased polar group may be a dominant factor inducing a hydrophilic surface.

For a more rigorous investigation, a series of experiments were conducted to modify the PS surface to either superhydrophobic or highly hydrophilic with different surface structures created on the surface as discussed in sections 7.4 and 7.5.

7.4 Hydrophobic modification

To have a hydrophobic surface from an initially hydrophilic surface, the surface must be sufficiently rough. A 3 mm x 3 mm surface area was scanned with the scanning speed varied from 1 mm/s to 12 mm/s. The fluence was fixed at 5.66 J/cm² with a shifting pitch of 0.02 mm. Micro-scale grooves were created on the sample surface with different laser parameters. The effect of scanning speed, which determines the number of pulses on each irradiated location, on the surface WCA was shown in Fig. 7.6. The surface became superhydrophobic (WCA of 156.2°) at 1 mm/s. Fig. 7.7 showed the SEM images of the sample surface structure irradiated under different scanning speeds.

Fig. 7.6 Effect of scanning speed on surface water contact angle.

Fig. 7.7 SEM images of surface structure at different scanning speed: (a) 1 mm/s, (b) 2 mm/s, (c) 3 mm/s (d) 4 mm/s and (e) 12 mm/s.

As shown in Fig. 7.7, grooves were observed on the surface, which was relatively rougher at the lower scanning speeds. It was observed that the groove structure

became shallower and smoother with increasing scanning speed. At 3 mm/s the groove ridges was no longer clearly defined. Furthermore, it was found that there was little variation of the surface structure with scanning speeds exceeding 4 mm/s. Fig. 7.7 (d) and Fig. 7.7 (e) showed surface structure at 4 mm/s and 12 mm/s with no significant difference between them. The surface roughness (Ra) at different scanning speed, and the pristine surface roughness (7.98 nm) are shown in Fig. 7.8. At the lower scanning speeds the surface is generally rough. For example, the surface roughness (Ra) is 9.54 μm and 4.01 μm at the scanning speeds of 1 mm/s and 2 mm/s respectively. Fig. 7.9 showed the WCA as a function of the surface roughness. It was observed that the WCA increased with an increase in the surface roughness, which can be explained by the Cassie-Baxter's model [145] that the liquid droplet does not completely wet the roughened substrate. When a surface was rough enough, air can be entrapped between the liquid and the solid. The interface becomes composite and the contact angle increases with roughness even if the surface chemistry was intrinsically hydrophilic.

Fig. 7.8 Effect of scanning speed on surface roughness. The pristine surface roughness is around 7.98 nm, which is indicated by the star in the figure.

Fig. 7.9 Effect of surface roughness on WCA. The star in the figure presents the WCA of pristine sample.

XPS analysis was conducted on the hydrophobic surfaces to examine the effect of surface chemistry on WCA. Fig. 7.10 showed the measured XPS spectra of a pristine surface and a superhydrophobic surface. The bond information was contained in Table 7.3.

Fig. 7.10 XPS spectra of (a) pristine PS surface and (b) laser treated PS surface at a scanning speed of 1 mm/s.

Table 7.3 Polar and non-polar groups of pristine PS and PS surface treated at different scanning speed.

Scanning speed (mm/s)	Non-polar groups C-C/H (at. %)	Polar group C-O (at. %)	Polar group C=O (at. %)	Sum of polar groups at 0 days (at. %)	Sum of polar groups after 1 month (at. %)	Water contact angle	Increase in water contact angle after laser treatment
0	100	-	-	-	-	88.2°	
1	82.69	14.23	3.08	17.31	17.25	156.2°	68°
2	76.44	16.98	6.58	23.56	20.68	147.9 °	59.7 °
6	67.44	28.42	4.14	32.56	23.49	108.8 °	20.6 °
9	73.32	23.91	2.77	26.68	21.98	123.6 °	35.4 °

As depicted in Fig. 7.10 and Table 7.3, the oxygen content (polar group) increased after laser treatment. The total polar groups (at.%) varied with the beam scanning speed, i.e. the beam-material interaction time. At the speed of 1 mm/s, the sum of the polar groups was 17.31 (at. %) and the WCA reached 156.2°, indicating a superhydrophobic condition. The corresponding surface roughness had a high value of 9.54 μm . The rougher surface textures enabled more air trapped between the liquid and the surface, and thus contributed to the superhydrophobic condition. This implied that for a rough surface, the effect of the polar groups on WCA was not the dominating factor and the surface roughness or the surface topography structure played a more significant role in the changes of the surface WCA. The changed WCA (mainly due to the surface structure) after laser treatment was shown in Table 7.2. It shows that the effect of surface structure on water contact angle was as high as 68° at a scanning speed of 1mm/s.

It is known that a hydrophilic surface, especially a superhydrophilic surface, tends to reduce its hydrophilicity over time, see for example section 7.5. As such, the WCA recovery of hydrophobic surfaces was also investigated, see Fig. 7.11. It presents the water contact angle of samples measured at different time after laser treatment, namely immediately after laser treatment (0 days), 3 days and one month after laser treatment. It can be observed that the hydrophobic property of the sample surface created by the laser treatment was rather stable, with no or negligible changes over time.

Examination of the surface structure indicates that it remained the same over time. In contrast, the surface polar groups were reduced over time as shown in Table 7.3. These results indicated that the surface structure dominated the surface wettability

at high roughness, and was rather insensitive to surface chemistry.

Fig. 7.11 Variation of WCA of laser treated sample over time at different scanning speed.

7.5 Hydrophilic modification

To have a hydrophilic surface, micro-scale pits were created on the PS surface. The PS surface was treated under a high scanning speed of 200 mm/s with the hatching distance fixed at 200 μm . The repetition rate was fixed at 1 kHz. A matrix of pits was created with a pitch density of 200 μm . The surface was treated under different fluence varied from 1.49 J/cm² to 193.94 J/cm². The effect of laser fluence on WCA was presented in Fig. 7.12.

As the laser fluence increased, the surface WCA decreased to highly hydrophilic (around 12.7°) from its original WCA of 88.2°. This was due to the created pits on the surface. The water droplet could easily penetrate into the surface with these surface pits. Thus, the surface became more hydrophilic. The effect of laser fluence

on the size and depth of the micro-pits was investigated as depicted in Fig. 7.13. With the fluence increased from 4.75 J/cm^2 to 36.62 J/cm^2 , the radius of pits increased from $8.86 \text{ }\mu\text{m}$ to $21.04 \text{ }\mu\text{m}$, and the depth of pit from $0.98 \text{ }\mu\text{m}$ to $2.79 \text{ }\mu\text{m}$. The increased size of pit had an effect on the water contact angle of PS surface, see Fig. 7.14. For instance, as the depth of pit increased from $0.98 \text{ }\mu\text{m}$ to $2.79 \text{ }\mu\text{m}$, the WCA decreased from 88° to 26.52° . Since the depth of pits was pretty small, in few microns, the material maintained high transparency after laser treatment. This will be discussed in details later.

Fig. 7.12 Surface water contact angle at different laser fluence.

Fig. 7.13 Effect of laser fluence on radius and depth of pits.

Fig. 7.14 Water contact angle and depth of pit vs laser fluence.

The effect of the pit matrix density on surface wettability was also investigated as shown in Fig. 7.15. The spacing between the pits was varied from 200 μm to 700 μm via varying the scanning speed from 200 mm/s to 700 mm/s. The water contact angle was varied from 15° to 80° as the spacing between the pits increased from 200 μm to 700 μm . Fig. 7.16 shows the structure of the created pits at a fluence of 4.75 J/cm².

Fig. 7.15 Effect of pit distance on surface WCA

Fig. 7.16 SEM image of (a) pristine sample surface and (b) micro-scale pits created on the sample surface after laser treatment.

One advantage of this method is that the material remains highly transparent after laser treatment as shown in Fig.7.17. Six areas inside the red rectangular were treated with different laser fluence: 193.94 J/cm², 169.53 J/cm², 130.20 J/cm², 86.53 J/cm², 48.42 J/cm², 23.06 J/cm², and these respectively resulted in water contact angle of 12.70°, 15.04°, 15.87°, 16.95°, 17.19° and 38.82°. The transparency of pristine PS was around 90% in the visible wavelength. After laser treatment, the transparency decreased to 85% to 89% in the visible wavelength as shown in Fig. 7.18.

Fig. 7.17 Laser treated area at fluence of 193.94 J/cm², 169.53 J/cm², 130.20 J/cm², 86.53 J/cm², 48.42 J/cm², 23.06 J/cm² (all included in the red rectangular area). Scanning speed was fixed at 200 mm/s with a 200 μ m hatching density. After laser treatment the sample became highly hydrophilic (as small as 12.70°), while the material transparency was maintained.

Fig. 7.18 Material transparency before and after laser treatment measured by a photo spectrometer (wavelength varied from 200 nm to 1500 nm).

It is known that a hydrophilic surface, especially a superhydrophilic surface, tends to reduce its hydrophilicity over time. Thus, the stability of WCA of the laser treated surface was investigated over time as shown in Fig. 7.19. The PS surface became highly hydrophilic (WCA of 12.7°) after laser treatment at fluence of 193.94 J/cm^2 ; after one month the WCA recovered to 63.7° . This is due to the slow reaction between surface and air. Thus XPS analysis of chemical bonds was conducted on the laser treated sample at a fluence of 193.94 J/cm^2 and laser treated sample at a fluence of 193.94 J/cm^2 after one month as shown in Fig. 7.20. The XPS analysis shows that the surface polar groups decreased to 15.43 at.% from 23.72 at.% after one month. Since the surface structure was examined to remain the same, the recovered 51° water contact angle can be attributed mainly due to the decreasing surface polar groups on the PS surface over time as presented in Table 7.4. The laser-induced WCA changes was 75.5° (WCA difference refer to pristine 88.2°). Deducting the effect of recovery, the effect of surface structure on WCA was calculated to be 24.5° . This implied that the surface WCA was determined by both surface chemistry and surface structure. The result was consistent with Wenzel's model. This observation was rather different from that of a hydrophobic surface, which was consistent with Cassie-Baxter's model and dominated by the rough surface structure and are relatively stable.

Fig. 7.19 Variation of WCA of laser treated sample over time. Laser treated sample at the fluence of (1) 193.94 J/cm², (2) 169.53 J/cm², (3) 130.20 J/cm², (4) 86.53 J/cm², (5) 48.42 J/cm² and (6) 23.06 J/cm².

Table 7.4 Polar and non-polar groups on PS surface over time. (1) pristine PS, (2) laser treated sample at 193.94 J/cm² at 0 days and (3) laser treated sample at 193.94 J/cm² after one month.

Sample No.	Non-polar groups C-C/C-H (at.%)	Sum of Polar groups C-O and C=O (at.%)	Water contact angle(°)	Increase in water contact angle (°)
1	100	-	88.2	
2	76.28	23.72	12.7	-75.5 (due to laser treatment)
3	84.57	15.43	63.7	+51 (due to recovery)

Fig. 7.20 XPS spectra of (a) pristine PS surface and (b) laser treated PS surface at a fluence of 193.94 J/cm^2 and (c) laser treated PS surface at a fluence of 193.94 J/cm^2 after one month.

7.6 Summary

In this chapter, femtosecond laser-induced surface wettability modification of PS has been investigated. The surface water contact angle at different z positions (and thus laser intensities) has been examined. At high laser intensity, the laser power absorption is high; the surface became very rough and hydrophobic. At low laser intensity, the surface became relatively much smoother and hydrophilic.

Based on these experimental observations, for a rough surface, the surface became hydrophobic and the wettability was mainly determined by the surface structure. When the surface was relatively smooth, the surface became hydrophilic due to the increase in surface polar groups.

A series of experiments had been conducted for the controlled modification of the PS surface to either hydrophobic or hydrophilic. In creating a superhydrophobic surface, micro-scale grooves were created on the sample surface. The surface roughness was as high as 9.54 μm in Ra after laser treatment, resulting in hydrophobic and even superhydrophobic ($\text{WCA} = 156.2^\circ$) surfaces. Air bubbles could well be trapped in between the sample surface and water droplets for these rough surfaces. Under these conditions, surface structure is the main factor that determining the surface wettability, and is consistent with the Cassie-Baxter's model. As a result, the surface wettability of hydrophobic surfaces was stable over time after laser treatment as the surface structure remained the same over time.

With properly spaced micro-pits created on the surface, the PS sample became more hydrophilic. The surface wettability increased with the depth, size and density of the micro-pits. This is consistent with Wenzel's model. Since the pit depth was shallow,

the substrate maintains high transparency after the laser treatment. The original substrate transparency to visible wavelength was around 90%. The substrate transparency after laser treatment was around 85% to 89% at the visible wavelength. WCA recovery was found on hydrophilic surfaces especially highly hydrophilic surfaces after laser treatment. This was mainly due to the decreased polar groups over time.

Chapter 8 Conclusions and future works

8.1 Conclusions

Ultrashort pulsed laser material processing is a complicated process which warrants an in-depth study. Despite the many investigations in recent years, there are issues yet to be clarified or resolved which include: a) a quantitative study of nonlinear absorption induced by femtosecond laser irradiation on a material which is transparent to the laser wavelength, in particular for a thick sample, b) thermal effects induced by femtosecond laser on a transparent material, c) heat conduction simulation within the substrate subsequent to nonlinear absorption, and d) surface wettability modification of polystyrene (PS) samples through laser irradiation.

As PS is transparent to the wavelength of the femtosecond laser used in this investigation, it is also a natural candidate for resolving issues outlined in (a), (b) and (c). As such, this investigation focuses on the followings:

(a) Nonlinear absorption induced by femtosecond laser irradiation on thick PS polymer which is transparent to the laser wavelength.

Nonlinear absorption is an important process as it is the first step of laser-material interaction. It can be expressed as:

$$\frac{dI}{dz} = (\alpha + \beta I)I \quad (2.19)$$

In this study, the nonlinear absorption behavior of PS samples irradiated by 795 nm femtosecond laser was investigated. PS was highly transparent to this laser wavelength with negligible linear absorption ($\alpha \approx 0$) as measured by a

photospectrometer. This allows the investigation to focus directly on non-linear absorption as a result of laser PS interaction.

This investigation represents a first attempt to quantify the nonlinear absorption coefficient of thick transparent PS sample for a wide range of laser intensity. z scan technique was applied to a thick PS sample (1.2 mm), which could be treated as a stack of thin layers. The nonlinear behavior at different laser powers: 5.2 mW, 10.4 mW, 14.4 mW and 23.5 mW were investigated. The nonlinear absorption coefficient of PS, which has never been determined previously, was determined to be 0.000695 m/W. Consistent with expectation, the results showed that as the laser intensity increased, the absorption increased while the transmittance decreased. In addition, for the laser intensities investigated, a single non-linear absorption coefficient was found to be adequate to describe the non-linear absorption process.

(b) Thermal effects induced by femtosecond laser on transparent material.

Subsequent to energy absorption, the absorbed energy was dissipated into the bulk material as heat. Thermal effects are important as they have effects on the machining precision and material property after laser treatment. In contrast to our group's previous investigations [35-37] on non-transparent materials, the current investigation focused on femtosecond laser interaction with PS, which is transparent to the laser beam employed. With an infrared camera properly calibrated with thermal couples for temperature measurements, the temperature changes during laser irradiation were directly measured.

For the same laser power employed, the overall temperature increase was much more significant when the sample was placed near to the focal position with high

laser intensity as compared with a sample placed further away from the focal plane. When the absorbed energy was subsequently conducted away as heat, it resulted in temperature increase of the sample. The higher temperature increase for sample at the focal plane thus indicates that there was more laser energy absorbed by the sample at the focal plane.

These experimental observations on the temperature fields of samples irradiated with different laser intensities are consistent with the nonlinear absorption observed in (a), namely higher laser intensity resulted in higher laser power absorption and thus higher sample temperature.

(c) Heat conduction simulation within the substrate subsequent to nonlinear absorption.

For a rigorous validation of the obtained nonlinear absorption coefficient, and the resulting temperature field subsequent to the absorption of laser power, the results obtained in (a) and (b) can be correlated. In this study, for the first time, a 3D FE model was constructed to simulate the temperature changes based on the nonlinear absorption observed in (a) and compared with experimental measurements in (b). The model was constructed with the sample divided into six thin layers with a layer thickness of 200 μm . Good agreement were obtained between the simulated and experimental results at $z = 2 \text{ mm}$ (with ablation) and $z = 4 \text{ mm}$ (without ablation) with less than 2% difference between them. In contrast, when the laser beam was focused at the sample surface ($z = 0$), the simulated temperature was higher than the experimentally measured results. The difference between the simulated and experimentally measured results was around 21.5%. This was due to the high laser intensity such that there was laser-induced ablation with plasma formation at the

surface at this high laser intensity. A simple energy balance to include energy consumed for material ablation indicated that only a small amount of energy was used for material vaporization during ablation. Instead, plasma generation during ablation was deduced to consume a significant amount of energy, and was the dominant factor in reducing the incident energy being absorbed and converted to heat by the substrate. This ionization energy for plasma formation could account for the discrepancy observed between simulation and observed temperature.

Indeed, heat conduction as a result of the absorbed laser power was significant and dominant, with or without ablation. Plasma shielding effect was calculated to be insignificant, which is consistent with the previous findings. The rather good correlation between the predicted temperature field based on the absorbed laser power and the experimentally observed temperature field provides an excellent validation on the obtained non-linear absorption coefficient and the associated approach.

(d) Surface wettability modification of PS samples through laser irradiation.

In addition to the investigation of laser polymer interaction and the associated non-linear absorption of power for a femtosecond laser, the application of the laser for polymer surface modification was studied. Wettability is one of the most important surface properties. Controlled surface wettability modification of polymers is highly desirable and has various applications. PS is a polymer with many applications, and hitherto there is no investigation on using laser for its controlled surface wettability modification. This investigation presents the controlled surface wettability modification of PS samples, and relates the resulting water contact angle (WCA) with laser intensity and its absorption.

The surface water contact angle at different z positions, and thus laser intensities and absorptions refer to (a), was studied. At high laser intensity, the laser power absorption is high; the surface became very rough and hydrophobic. At low laser intensity, the surface became relatively much smoother and hydrophilic.

For a rigorous investigation, a series of experiments were conducted to modify the PS surface to either superhydrophobic or highly hydrophilic with different surface structures created on the surface. It was found that with micro-scale grooves created on the sample surface, the surface became very rough (Ra as high as 9.54 μm) resulting in hydrophobic and even superhydrophobic (WCA = 156.2°) surfaces. Air bubbles could be trapped in between the sample surface and water droplets for these rough surfaces. Under these conditions, surface structure was the mainly factor that determining the surface wettability, and was consistent with the Cassie-Baxter's model. The surface wettability of hydrophobic surfaces was examined to be stable over time after laser treatment as the surface structure remained the same over time.

With properly spaced micro-pits created on the surface, the PS sample became more hydrophilic due to the ease of penetration of water droplets into the micro-pits. The surface wettability increased with the depth, size and density of the micro-pits. This was consistent with Wenzel's model. Since the pit depth was shallow, the substrate maintains high transparency after the laser treatment. After laser treatment, WCA recovery was found on hydrophilic surfaces, especially on highly hydrophilic surfaces. This was due to the decreased polar groups over time.

8.2 Recommendations for future work

For further studies and investigations, the followings are recommended:

- 1) Nonlinear laser energy absorption of thick polystyrene has been studied in this investigation. Similar investigation can be conducted for other transparent polymers, or other semi-transparent materials such as glasses and silicon. Their behavior may be different from polymers as they have different structures and material properties. In addition, the nonlinear absorption behavior was analyzed with a semi-analytical method in the current investigation. Numerical method may be employed as it is more versatile and could investigate other assumed non-linear relationship or function for non-linear laser energy absorption.
- 2) Current simulation only focused on heat conduction. Material ablation at high laser power was not considered. The model may be improved to include laser-induced material ablation in future studies.
- 3) Experimental observations indicated that the WCA of hydrophilic surface tends to recover to its original water contact angle overtime. For future studies, the effects of various controlled ambient environments on WCA recovery can be investigated. At different environments such as water, ethanol, and different gases, the recovery rate may be different.
- 4) Current experimental findings indicate that for a rough surface, the surface structure is the dominant factor on surface wettability. Future work may include the investigation on the effect of different surface patterns on surface wettability. For instance, pillars, cylinders and pits may be created on the surface. The effect of the size (height, diameter and density) of these created structures on surface wettability can be investigated.

5) As commercial polymers have various additives depending on the suppliers, it will be of practical values if polystyrenes from various suppliers are investigated to ascertain the sensitivities of the results obtained in this investigation to these additives.

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Appendix A: Energy calculations for material ablation for chapter 6

As depicted in chapter 6, material ablation can be estimated by considering the vaporization and ionization energies required.

Vaporization energy

The vaporization energy consists of two components: energy consumed by the material to vaporize and the energy for heating up the material to the vaporization temperature. It can be calculated as:

$$E_{vap} = H_{vap} * V * \rho + Cp * V * \rho * \Delta T \quad (6.16)$$

Where H_{vap} is the energy consumed for the material to burn out, which is around 1000 J/g, based on the differential scanning calorimetry (DSC) method [137]. V is the ablated material volume, ρ the material density which is 1050 kg/m³, Cp the material heat capacity which is 1200 J/kg·K and ΔT the temperature difference (approximately equals to 400 °C) [137]. The vaporization temperature is at 427 °C [137].

To calculate the ablated material volume V , the laser ablated hole may be treated as a cone and the ablated volume can be calculated by:

$$V = \frac{1}{3} h \pi r^2 \quad (A1)$$

Where h is the height of the hole, and r is the base radius of the hole (cone).

For the experiment conducted at $z = 0$ mm

Through image analysis of Figure 6.11 (a) (shown below) in chapter 6 using a commercial software image J, h is estimated to be around $189.66 \mu\text{m}$ and r $25.00 \mu\text{m}$., defining approximately the ablated “cone” shown as white lines in the figure. Using equation A1, the ablated volume is calculated to be around $1.24 \times 10^5 \mu\text{m}^3$.

Figure 6.11 (a) Cross section view of sample at $z = 0$ mm at a laser power of 8.47 mW with irradiation time of 20s. The ablated edge is shown as red dotted line. The approximated cone is shown in white line.

Using equation 6.16, for this ablated volume, the vaporization energy is estimated to be around 1.93×10^{-4} J. With the laser incident power at 8.47 mW over an irradiation time of 20s, the laser incident energy is 1.69×10^{-1} J. Thus the % energy used for material vaporization can be calculated as 1.93×10^{-4} J / 1.69×10^{-1} J, which is around 0.11 %.

At $z = 0\text{mm}$, the laser intensity is as high as $1.2 \times 10^7 \text{ W/m}^2$. Plasma may be generated during the experiment, indicating that ionization energy is consumed during ablation. The ionization energy is calculated based on the element ionization energy [138, 139]. The molecular expression of polystyrene is $(\text{C}_8\text{H}_8)_n$ with a mer molecular weight of 104 g/mol [140]. With only two elements, namely hydrogen and carbon, the ionization energy may be calculated by:

$$E_{ion} = M_H ION_H + M_C ION_C \quad (6.17)$$

Where M_H is the mole of hydrogen atom, ION_H the ionization energy of hydrogen atom in kJ/mole , M_C the mole of carbon atom, ION_C the ionization energy of carbon atom in kJ/mole . All the ablated material is assumed to be ionized to plasma. For hydrogen, the first molar ionization energy was considered (1312 kJ/mole), and for carbon the 3rd molar ionization energy (4620.5 kJ/mole).

With an ablated volume of $1.24 \times 10^5 \mu\text{m}^3$ and a material density of 1050 kg/m^3 , the mass of ablated material is calculated to be $1.30 \times 10^{-7} \text{ g}$. The mer molecular weight of polystyrene is 104 g/mol [140]. The mole of polystyrene ablated is therefore around $1.25 \times 10^{-9} \text{ mol}$. The molecular expression of polystyrene is $(\text{C}_8\text{H}_8)_n$. Thus, 1 mole of polystyrene contains 8 mole of hydrogen atoms M_H and 8 mole of carbon atom M_C , i.e $8 \times 1.25 \times 10^{-9} \text{ mol} = 1.00 \times 10^{-8} \text{ mol}$.

Using equation 6.17, the ionization energy is calculated to be $0.59 \times 10^{-1} \text{ J}$. As calculated, the total laser incident energy is $1.69 \times 10^{-1} \text{ J}$. Thus, the % of energy used for ionization is $0.59 \times 10^{-1} \text{ J} / 1.69 \times 10^{-1} \text{ J} = 34.91\%$ of the laser incident laser energy.

For the experiment conducted at $z = 2$ mm

The calculation procedure is similar as $z = 0$ mm. Through image analysis of Fig.6.11 (b) (shown below) in chapter 6 using a commercial software image J, h is estimated to be around $44.64 \mu\text{m}$ and r $51.79 \mu\text{m}$. defining approximately the ablated “cone” shown as dotted lines in the figure. Using equation A1, the ablated volume is calculated to be around $1.25 \times 10^5 \mu\text{m}^3$.

Figure 6.11 (b) Cross section view of sample at $z = 2$ mm at a laser power of 8.47 mW with irradiation time of 20s. The ablated edge is shown as red dotted line. The approximated cone is shown in white line.

For this ablated volume, the vaporization energy is estimated to be around 1.95×10^{-4} J using equation 6.16. With the laser incident power at 8.47 mW over an irradiation time of 20s, the laser incident energy is 1.69×10^{-1} J. Thus the % energy used for material vaporization can be calculated as $1.95 \times 10^{-4} \text{ J} / 1.69 \times 10^{-1} \text{ J}$, which is around 0.12 %.

Although at $z = 2$ mm, there were material ablation similar to that at $z = 0$ mm. However, at $z = 2$ mm most of the absorbed energy are transferred to the bulk material as heat as shown in Table 6.2 in chapter 6. Thus, it can be assumed that there is no or negligible plasma formation in this case. This is because at $z = 2$ mm, the laser beam is defocused, and the laser intensity (average laser intensity of 2.0×10^6 W/m²) is much lower than the focused laser beam at $z = 0$ mm (average laser intensity of 1.2×10^7 W/m²). This defocused beam can be observed through the much larger radius (r) of the ablated cone at $z = 2$ mm. As such, it is assumed that there is no ionization consumed during ablation.

For the experiment conducted at $z = 4$ mm

At $z = 4$ mm, the energy absorption and the temperature increase are much less than that at $z = 0$ mm and $z = 2$ mm. From Table 6.2 in chapter 6, it can be observed that almost all the absorbed energy is transferred to the bulk material as heat. As shown in Fig. 6.11 (c) (shown below), no obvious ablation was observed. The vaporization energy and ionization energy were negligible.

Figure 6.11 (c) Cross section view of sample at $z = 4$ mm at a laser power of 8.47 mW with irradiation time of 20s.