LASER MICROMACHINING OF A BIODEGRADABLE POLYMER

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ABSTRACT

This paper reports on UV laser micromachining of a biodegradable polymer for applications in biomedical engineering. Parametric studies have been conducted on Poly-vinyl Alcohol (PVA), a biodegradable polymer, to produce micro channels and micro holes. Laser micromachining of micro channels is studied using a XeCl excimer laser at 308 nm wavelength and laser micro drilling is studied using a Q-switched Nd: YAG laser at 266 nm wavelength. Feature sizes ranging from 4 to 10 μm were obtained for the micro holes and the features of micro channels ranged from 33 to 65 μm wide and 22 to 123 μm deep. This work demonstrated that UV laser micromachining is a well-suited technique for biodegradable polymers with minimum thermal damage to the surrounding material.

INTRODUCTION

In the field of biomedical engineering, micro devices such as implantable drug delivery systems are currently being developed. At present the substrate materials used for fabricating most of the micro devices are silicon or glass using IC (integrated circuit) techniques [1]. A major disadvantage of any nonbiodegradable device is that it must be removed surgically once the drug is exhausted [2]. It is advantageous to design and fabricate such micro devices using biodegradable polymers because they would naturally degrade and disappear in the tissue over a period of time. Biodegradable systems on the other hand, should be thoroughly checked from the toxicological point of view with regard to their effect on tissue and the mode of metabolism. Currently some of the biodegradable drug delivery systems find applications in fertility control, treatment of narcotic addicts, and antimalarials [3].

PVA is one of the important biodegradable polymers used in biomedical engineering. The chemical structure of PVA is [--CH_2 --CHOH--]. It is a water-soluble polymer and has excellent physical properties. It is used in wide range of applications such as adhesives, fibers, textile, paper sizing, and water-soluble packaging.

Most of the conventional techniques are not suitable for processing micro scale patterns on biodegradable polymers. Electron beam etching techniques produce too much heat and damage the polymer very fast [4]. Techniques like atomic force microscopy (AFM) that utilize mechanical forces to etch the surface are very slow and can not be used reliably and conveniently to etch large surface areas [5]. Therefore, there is an acute need for new state-of-the-art techniques to avoid problems associated with the current techniques. A technique that is clean, environmentally benign and less thermal damage is necessary to process the biodegradable polymer. Laser micromachining makes it possible to pattern biodegradable polymers on the micro scale unlike the difficulties associated with the above conventional methods. Some of the advantages this technique offers are non-contact clean process, absence of chemicals, single-step processing, high precision and repeatability, flexible feature size and shape.

Laser micromachining has been conducted on various materials such as metals, semiconductors, ceramics, and some polymers for numerous applications in engineering [6]. Micromachining of polymers is an important field that has both immediate and future applications in diverse fields such as medicine, Micro Electro Mechanical Systems (MEMS), and photonics. There is a growing interest in the precise fabrication of microstructures in the field of biomedical engineering such as drug delivery systems, implants, and catheters. Much work has been conducted on various kinds of polymers such as Polymethylmethacrylate (PMMA), Polypropylene (PP), Polyamide (PI), etc. However, no work has been reported on processing of biodegradable polymers on the micro scale, regardless of the increasing demands of biodegradable micro devices for applications in biomedical engineering.

The wavelength of the laser is an important parameter for micromachining of polymers. When fabricating devices for applications in biomedical engineering, care should be taken to minimize the thermal damage to the device. Micromachining with nanosecond green or infrared lasers have strong thermal effects [7], whereas the UV wavelength range offers higher photon energy to break the material chemical bonds directly without significant heat transfer to the surrounding material. This important feature makes UV laser micromachining very attractive for biodegradable polymer materials since thermal damage to the non-machined part can be minimized.

The work reported here investigates the micromachining of a biodegradable polymer by UV laser irradiation. XeCl-excimer laser (308 nm) and Nd: YAG laser (266 nm) is used to produce micro channels and micro holes on a PVA substrate respectively. Micro channels find applications in nerve regeneration of biomedical research. The nerve cells have the ability to recognize three-dimensional structures and these 3-D micro channels act as a bridge to guide the damaged nerves to grow back together. An array of micro holes is drilled on the polymer, which is used as a biodegradable filter for biomolecular separation. This work on laser UV micromachining of a biodegradable polymer for applications in biomedical engineering is the first of its kind.

THEORETICAL BACKGROUND

There has been much uncertainty and debate over the fundamental ablation mechanisms in polymers. Several photochemical and photo thermal models have been developed to explain the ablation mechanisms. In photochemical mechanism the photon energy of the light is used to break the chemical bonds of the polymer directly where as in photo thermal mechanism the material is ablated by heating, melting and vaporizing the material [8].

It is found that the material removal by laser ablation approximately obeys the Beer Lambert's law at lower laser fluences [9]. The relation between the etching depth and intensity of the laser is given by,

$$L_f = (1 / \alpha) \ln (F / F_{th}). \quad (1)$$

Where,

L_f = Etch depth per pulse (μm).
α = Absorption coefficient (cm $^{-1}$).
F = Induced fluence (J / cm^2).
F_{th} = Threshold fluence (J / cm^2).

For photochemical ablation to occur, energy of the photons at that wavelength should overcome the intermolecular bond energies of the polymer. The relation between the photon energy of light and laser wavelength is given by,

$$E = 1.245 / \lambda \quad (2)$$

Where,

λ = Wavelength of light (μm)
E = Energy of photons (eV)

The photon energy of the light depends on the wavelength of the light and as the wavelength increases the photon energy decreases. An UV laser with a wavelength of 266 nm has photon energy of 4.66 eV. Typically the C-C bond energy is 4.6 eV and C-H bond energy is 4.2 eV in polymers. It can be seen that for photochemical ablation to occur in polymers the photon energy of the light should be greater than the bond energy of the material.

Garrison and Srinivasan [10] presented a photochemical model, which is based on a volume change of the material after the photolysis, induced by the UV radiation. A photochemical-thermal model was developed by Srinivasan et al [11] in which a thermal contribution to etching is added to the photochemical contribution derived from low fluence measurements. Several other theories to explain the ablation mechanism have surfaced considering issues such as, three state chromophores, refractive index of polymer, microroughness, random polarization and weak focussing of the beam etc [12]. Other theoretical models include dynamic model, receding surface treatment, chromophore bleaching, plume screening, and Arrhenius type thermal activation.

EXPERIMENTAL PROCEDURE

All the experiments were performed in air. Figure 1 illustrates the experimental setup of the laser used for micromachining of the biodegradable polymers. The specifications of the excimer laser used in this study are given in Table1.

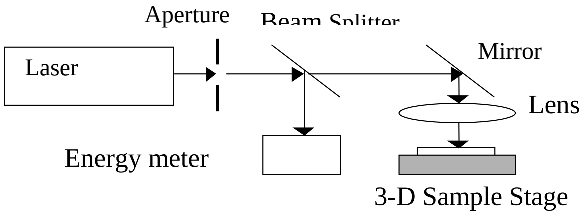

Figure 1 Schematic experimental setup.

Table 1
Specifications of the Excimer Laser

Medium	XeCl
Wavelength	308 nm
Pulse energy	150 mJ
Repetition rate	0.1 – 30 Hz
Pulse width	10 ns

A rectangular beam aperture shapes the excimer laser beam for producing the micro channels. The beam is then split into two using a 90/10 beam splitter, 10% of the beam is directed to power meter for measuring the energy and the 90% of the beam is directed to the polymer for machining. A cylindrical lens of 2-inch focal length is used to focus the laser beam onto the polymer. The polymer is mounted on a 3-D stage of a micrometer resolution. Multiple pulses were needed to ablate the polymer and a repetition rate of 1 Hz is maintained throughout the experiment.

A similar setup was used for drilling holes on the polymer sample using a Nd: YAG laser. A circular aperture is used to shape the beam and a spherical lens of 1-inch focal length is used to focus the beam. The specifications of this laser are given in Table 2.

The thickness of PVA samples ranged from 90 μm to 170 μm thick. Irradiation was done with excimer laser for channels and with Nd: YAG laser for holes. In laser ablation the experimental parameters that determine the features are the laser intensity, laser wavelength and number of pulses.

Table 2
Specifications of the Nd: YAG Laser

Medium	Nd: YAG crystal
Wavelength	266 nm
Pulse energy	35 mJ
Repetition rate	1 – 10 Hz
Pulse width	6-7 ns

The threshold energy, minimum energy required to ablate the polymer is found out. Multiple pulses above the threshold fluence were used to target the sample for ablation to occur. The etching depths per pulse were calculated by dividing the total etch depth by total number of pulses targeted. The size of micro channels is measured using a surface profilometer. An optical microscope and a scanning electron microscope (SEM) are used to study the characteristic features of the micro holes, micro channels and the changes in the surrounding material.

RESULTS AND DISCUSSION

Micro Holes

The PVA samples used were 90 μm thick. Threshold intensity for drilling holes on the polymer was found to be 0.2 mJ. The etching depths per pulse are calculated. The absorption coefficient (α) is obtained from the slope of the curve in Figure 2. At 266 nm wavelength, the absorption coefficient (α) was found out to be 0.834 x 10^4 cm^{-1}.

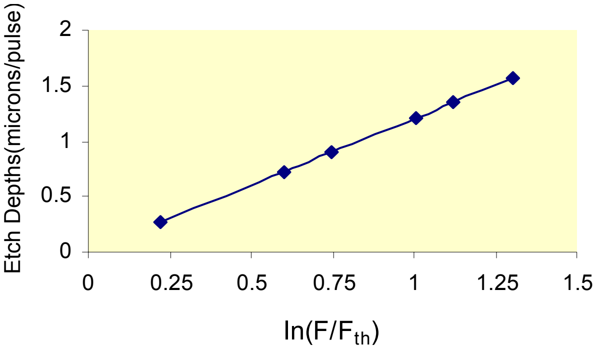

Figure 2. Etching depths Vs ln(F/F_{th}) for holes at 266 nm wavelength

Figure 3 shows PVA sample of 90 μm thick drilled at 0.735 mJ. A hole of 5.36 μm diameter is obtained for 100 pulses at the exit of sample. For energies varying from 0.5 mJ to 6.0 mJ the hole sizes ranging from 4 μm to 70 μm were observed on the exit of the sample. The radius of the beam on the surface of the sample is 12.5 μm. Holes observed on the entry of the sample were larger. Fine adjustments to the hole size were able to make by regulating the exact number of pulses delivered to the target. The taper of the hole along the thickness of the sample is around 6.5 degrees.

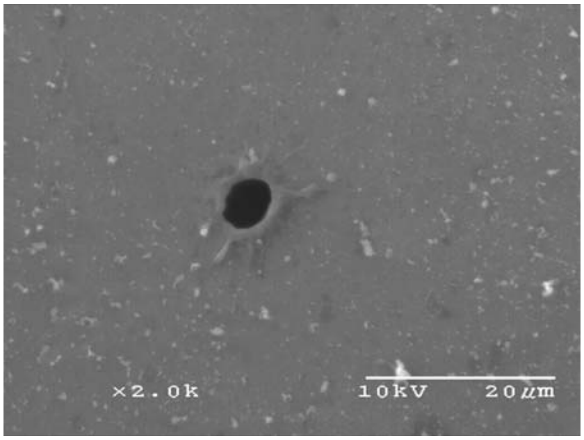

Figure 3. SEM image of 5.36 μm hole (at exit) drilled at 0.735 mJ

It is observed that the polymer is ablated layer by layer upon multi-pulse irradiation. As the thickness of the sample is increased, more number of pulses was required to get a through hole. Figure 4 illustrates the effect of laser energy on the hole diameter. As the energy is increased hole diameter is increased accordingly.

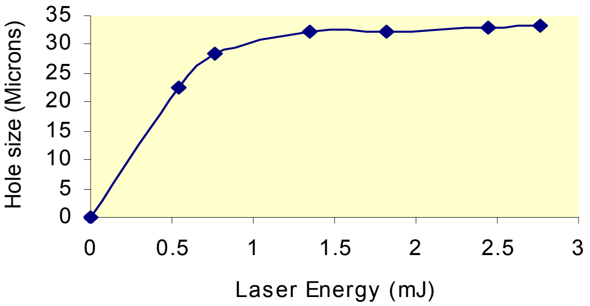

Figure 4. Laser energy Vs hole size

This is because the laser beam intensity has a Gaussian distribution. At 266 nm wavelength, very few thermal damages has been observed. The irregularities in the hole shape can be attributed to the spherical aberration and non-circularity of the laser beam. An array of holes is shown in Fig 5.

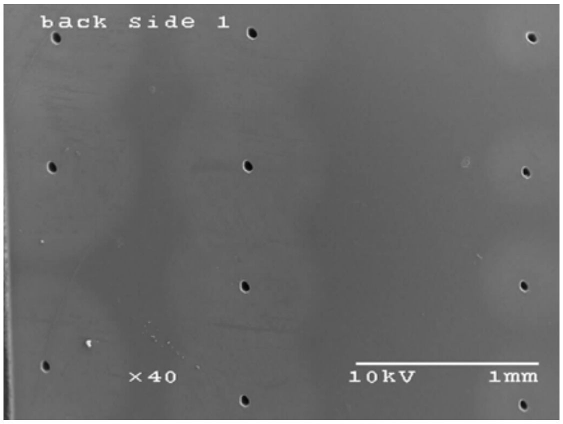

Figure 5. SEM image of an array of holes drilled in PVA at different laser energies.

Micro Channels.

Micro channels ranging from 33 to 65 μm wide and 22 to 123 μm deep has been micromachined with an excimer laser at 308 nm. Figure 6 shows the relation between etching depths and logarithm laser fluences.

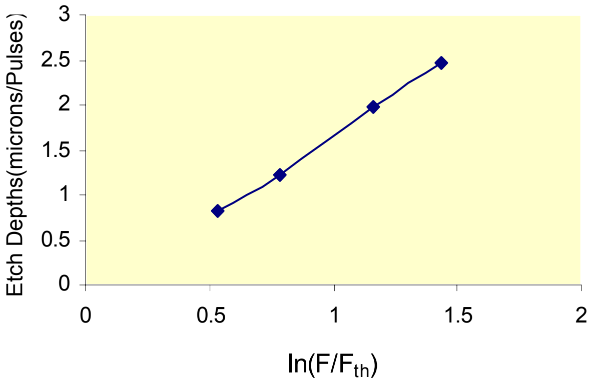

Figure 6. Etching Depths Vs $\ln(F/F_{th})$ for channels at 308 nm wavelength

The absorption coefficient was found out from the slope of the curve in Figure 6. At 308 nm the absorption coefficient (α) for PVA was found out to be 0.4×10^4 cm^{-1}. It is observed that, below the threshold energy there is no sign of ablation and above the threshold energy there is a linear relationship between the energy and the etching depths for the laser energy used in this study. Figure 7 shows micro channels etched at 17 and 22 mJ with 50 pulses. Distinct edges can been seen and the depth of channels was uniform along the length.

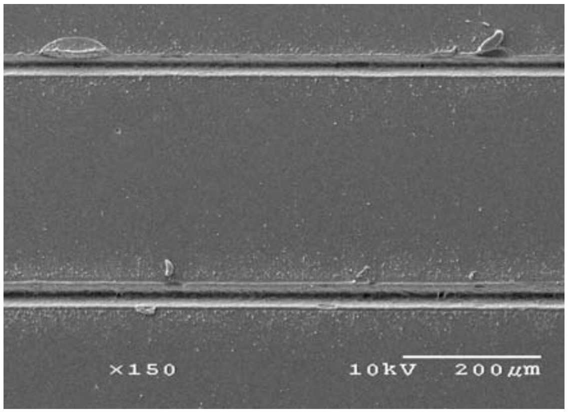

Figure 7. SEM image of Microchannels etched at 17 mJ (top) and 22 mJ (bottom).

Figure 8 shows the micro channels etched on PVA with an excimer laser. Micro channels shown are patterned with different laser energies. At 308 nm wavelength, the photon energy of light is about 4.02 eV. This energy is not sufficiently high enough to break the polymer bonds, so thermal contribution for ablation plays a role in ablating the material. Using a shorter wavelength laser could minimize these thermal effects of ablation. Excimer laser with a wavelength at 193 nm (6.26 eV) or 248 nm (5.0 eV) would be a good choice because the photon energy is much larger than the material chemical bond energy.

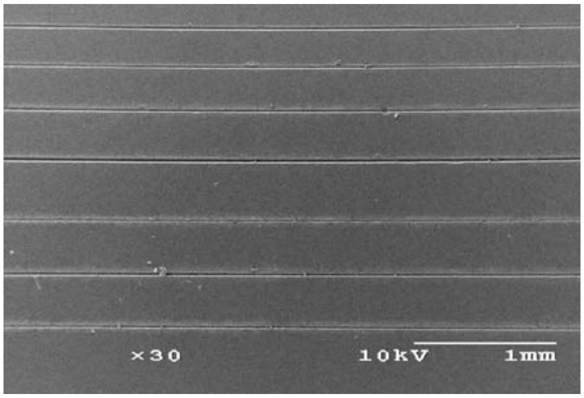

Figure 8. SEM image of Microchannels etched on PVA at 308 nm.

Excimer laser is best suited for micromachining channels because of its uniform rectangular beam shape.

SUMMARY

A biodegradable polymer has been micromachined by UV laser irradiation for applications in biomedical engineering. A Nd: YAG laser of 266 nm wavelength has been used to fabricate a biodegradable filter with an array of 5 μm holes to be used for biomolecular separation. Micro channels were produced by an excimer laser of 308-nm wavelength that finds applications in nerve regeneration. Less thermal damages have been observed around the holes and channels, which is very important for applications in biomedical engineering. The effect of ablation process on the polymer biodegradability is currently being studied. This work on biodegradable polymers for applications in biomedical engineering is first of its kind and it demonstrated that UV laser is well suited for micromachining of biodegradable polymers.

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