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Fabrication of Biodegradable Polymeric Micro-Devices Using Laser Micromachining

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Abstract. **Laser direct writing and percussion-drilling techniques are employed to fabricate two biodegradable micro-devices for biomedical engineering applications. Biodegradable polymeric material, poly-D-lactic acid (PDLA), and polymer poly-vinyl alcohol (PVA) were micropatterned by ultraviolet lasers. The morphology, dimensional accuracy, and surface conditions of the fabricated micro-devices after the laser ablation were studied using a scanning electron microscope (SEM) and a surface profilometer. The experimental results for producing micro-devices are reported. This work on laser micromachining of a biodegradable polymer for applications in biomedical engineering is the first of its kind and demonstrated that this technique is well suited to produce biodegradable microdevices with minimum thermal damage to the surrounding material.**

Key Words. **laser micromachining, polymeric micro-device, biodegradable polymers, micro-channel, micro-hole array**

1. Introduction

Implantable medical devices are currently fabricated from non-biodegradable materials like silicon, glass (Armani et al., 1999), and plastics (Lin et al., 1999). One of the major problems associated with these nonbiodegradable devices is that they must be removed surgically once the drug is exausted. Biodegradable polymers hold great promise as new materials for implantable biomedical micro-devices, due to their biocompatibility and natural ability to degrade in tissue over time. The advances in biodegradable polymer science are paving way for fabrication of implantable biodegradable micro-devices such as drug delivery systems (Karsten, 1998), tissue engineering (Curtis, 2001) and catheters in the field of biomedical engineering. Some of the commercial biodegradable devices available are sutures, dental devices, Orthopedic fixation, and guided tissue.

PDLA and PVA are excellent materials for implantation because PDLA degrades completely in the body by hydrolysis and PVA also dissolves in the body. These polymers have unique features such as controllability of mechanical properties, tailoring of degradation rates, and minimal toxicity and immune response that make them ideal for medical use. Micro-patterning these biodegradable polymers could provide guidance to the neurons at the cellular level surfaces (Meek et al., 1996). PVA membranes were fabricated by an UV laser for possible applications in bioseparations. PVA was chosen because of its hydrophilic nature, and these membranes are expected to minimize membrane fouling due to protein adsorption (Amada et al., 2000).

Micropatterning of polymeric materials is conducted by many methods and techniques. However, techniques such as electron beam etching produces too much heat and damage the polymers while photolithography involves multiple process steps and chemical solvents in the process (Matsui et al., 1995). Properties of biodegradable polymers degrade easily with chemical solvents or thermal impact. Moreover, after fabrication the residual chemical agents on the polymer surface could be toxic to the cells if using chemical etching. Atomic force microscopy (AFM), which is very slow and cannot be used conveniently to etch large surface areas (Ganepalli et al., 1998), utilizes mechanical forces to etch the surface. Non-photolithographic techniques, such as soft lithography techniques, have been developed for polymer microfabrication (Xia and Whitesides, 1998; Deniz et al., 2000). Soft lithography techniques include microcontact printing, micromolding in capillaries, microtransfer molding and replica molding, imprinting, and injection molding. However, the utility of these techniques is often limited by the availability of appropriate masters. A novel technique that is clean, environmentally benign, and creates little thermal damage to biodegradable polymers is needed for micro- and nano-fabrication of biodegradable micro-devices, and lasers can play an important role. Laser micromachining makes it possible to pattern biodegradable polymers on the micro-scale, unlike the difficulties associated with the above techniques. Photons are regarded as ''clean particles,'' and the laser irradiation is essentially non-invasive and a single-step process.

Micromachining with nanosecond green or infrared lasers has strong thermal effects (Chen et al., 2000), 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. In the UV region of the spectrum, the absorption of a photon by an organic molecule leads to an electronically excited state and bond breaking within the long chain polymer molecules occurs. This is followed by an audible shockwave and depending upon the wavelength and energy of the photons, the material is etched away with a geometry that is defined by the laser beam. The ejected material is decomposed polymer fragments, small particulate matter, and gases such as CO_2, C_2, and CO (Srinivasan et al., 1990). A pressure accompanies the ejection process of the polymer fragments that force away any debris accumulated in the ablated region. The train of multiple pulses also helps to blow out any debris inside the patterned features.

In this work, biodegradable polymers are micro-machined by UV lasers for applications in biomedical engineering. The work reported here investigated the micromachining of PDLA and PVA polymers by an excimer laser and an Nd : YAG laser. A 308 nm Xe-Cl excimer laser is used for producing microchannels for potential applications supporting peripheral nerve generation. A frequency quadrupled Nd : YAG laser at 266 nm was used to fabricate an ultrafiltration membrane for potential applications in molecular separations. The micro-features are characterized by a scanning electron microscope (SEM) and a surface profilometer.

2. Experiments

2.1. Laser micromachining setup

Figure 1 shows the schematic diagram of the laser micromachining setup. The laser micromachining set-up consisted of four main parts: a laser system, a beam delivery system, a micrometer-resolution x–y sample stage, and an on-line monitoring system. Two laser systems (excimer laser and Nd : YAG laser) were used in this work to demonstrate the micropatterning of polymers. The beam delivery system consisted of a couple of mirrors and lenses to guide and steer the beam for micromachining. The laser beam was split by a beam splitter. A small part of the beam was sent to the energy meter, and a major part of the beam was sent through the focusing lens to process the polymers. An objective lens was used to drill micro-holes, and a cylindrical lens was used to produce micron-size channel type patterns. A charged-coupled device (CCD) camera coupled with a TV monitor was used to capture the image around the machined area.

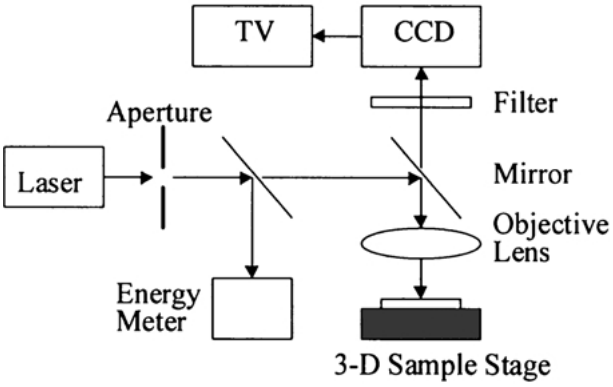

Fig. 1. Schematic laser set-up for micromachining polymers.

2.2. Materials and methods

The peripheral nerve regeneration device is a multi-layered polymer structure where PVA is cast over PDLA films. Compression-molded films of PDLA are obtained by compressing solid PDLA powder in a Carver press at 200-psi pressure at 50°C for 10 minutes. A solution of PVA in water (20% w/v) is cast over these films (50 μm) for the direct etching studies. PDLA films will degrade in about 4 to 6 months, depending on the copolymer ratio, while PVA films will dissolve in about 2 weeks at 37°C. The PVA will provide a hostile environment for laminin and cell adhesion, forcing the cells in the grooves. Direct etching of PDLA coated with PVA is carried out to selectively attach laminin to the PDLA underneath as shown in Figure 2.

A Xe-Cl excimer laser (Lambda Physik 308 EMG, 308 nm, pulse width = 10 ns, and repetition rate = 0.1−30 Hz) was used to irradiate the polymers to fabricate microchannels. The initial beam size of $10 \times 20\,mm^2$ was chopped down using a rectangular mask to shape the excimer laser beam to obtain straight and uniform channels. Lenses with 1-inch and 2-inch

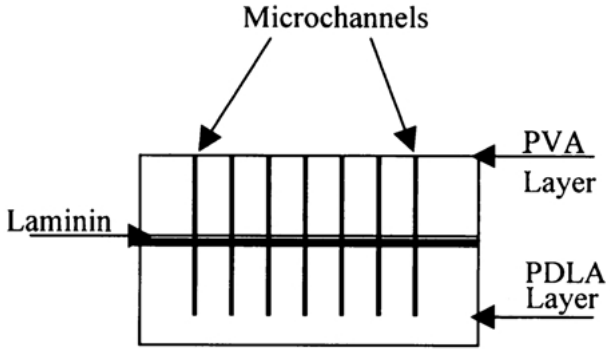

Fig. 2. Design of the multilayer biodegradable device for peripheral nerve regenerations.

focal lengths were used to obtain microchannels with different width grooves. The samples were ablated at the focal point as well as at the defocus plain. A frequency quadrupled Nd : YAG at 266 nm (35 mJ/pulse, pulse width = 6 ns, and repetition rate = 1–10 Hz) was used to fabricate microhole array. A circular mask was used to shape the beam. All the experiments were conducted in ambient air and at 1 Hz pulse repetition rate.

2.3. Feature characterization

SEM was used to study the topology and quality of the polymers after laser ablation. A surface profilometer (KLA Tencor, Alpha-step 100) was used to scan across the etched microchannels to get the cross-section profile and the depths of microchannels.

3. Results and Discussion

It was found that the material removal by laser ablation approximately follows Beer Lambert's law at lower laser fluences as used in this work. The relationship between the etching depths per pulse and the laser fluence is given by Srinivasan et al. (1982)

$$L_f = (1/\alpha)\ln(F/F_{th}), \tag{1}$$

where L_f = etch depth per pulse (μm), α = absorption coefficient (cm^{-1}), F = laser fluence (J/cm^2), and F_{th} = threshold fluence (J/cm^2). The threshold energy is the minimum energy needed to initiate the ablation process and energy below this threshold energy was absorbed as heat into the material. The parameters L_f, F, F_{th} are determined experimentally, independent of the equation. The slope of the graph plotted for L_f and F/F_{th} gives the absorption coefficient value for that specific polymer. The α of the polymer varies with the wavelength of the laser used. Multiple pulses were required to etch deep microchannels and microholes. The factors that determine the quality and feature size of machined features are based on experimental parameters such as fluence, wavelength, number of pulses delivered to the target, and beam focus.

3.1. Fabrication of microchannels

The fabrication of microchannels through the multilayer device involved studying the laser ablation rates for PVA and PDLA polymers individually. Both the polymers were ablated using an excimer laser. The polymers exhibited different absorption coefficient at the same wavelength (308 nm). The polymers had different threshold fluences; but by choosing a specific fluence, as well as a precise number of pulses to control the width and depth of the channels, it was possible to control

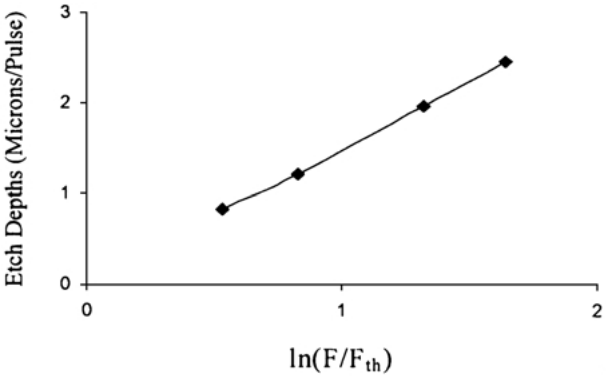

Fig. 3. *Relation between etching depths and logarithm of fluence for microchannels at 308 nm wavelength.*

fabrication of the microchannels. Figure 3 illustrates the effect of fluence on the etching depths at 308 nm for the PDLA polymer. The slope of the graphs gives the absorption coefficient of $0.4 \times 10^4 cm^{-1}$ for PDLA at this wavelength. The threshold fluence for the PDLA polymer was found to be around 0.5 mJ and the etching rate was also found.

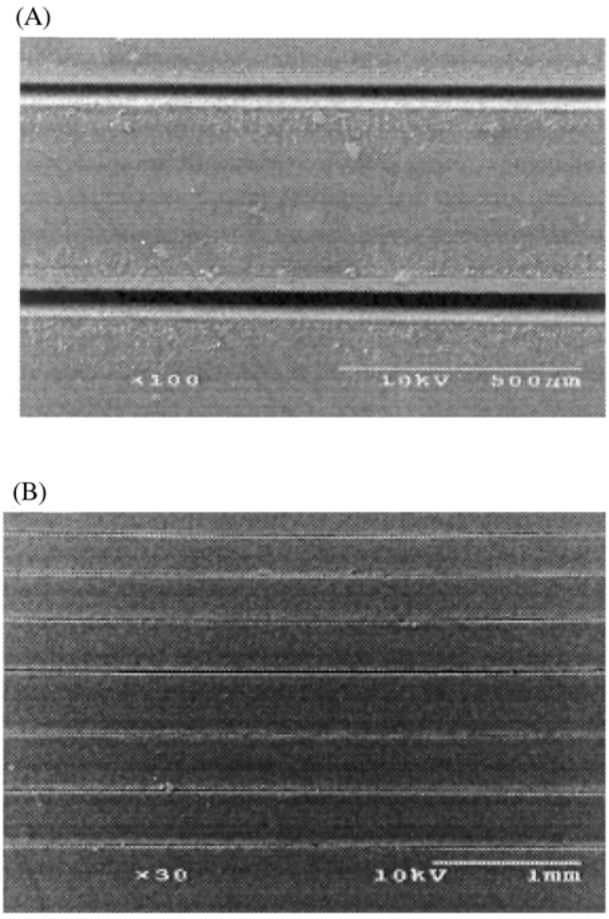

Fig. 4. *(A) Microchannels etched in PDLA at 308 nm wavelength, and (B) Array of microchannels etched in PDLA at various energies.*

Figure 4 shows the SEM micrographs of microchannels fabricated in the PDLA polymer. The structures in the SEM micrographs show straight vertical walls, and it was observed that the etching depths along the length of channels were constant.

3.2. Fabrication of ultrafiltration membranes

The ultrafiltration membranes were fabricated by drilling an array of predefined holes with specified hole dimensions. Percussion drilling was employed in fabricating these microfilters. The samples were flat and 90 μm thick. Figure 5 illustrates the effect of fluence on the etching depths at 266 nm for the PVA polymer. The threshold fluence for the PVA was found to be around 0.2 mJ at 266 nm wavelength. The etching depths plotted against the logarithm of fluence gave the absorption coefficient of PVA at 266 nm, which was found to be $0.834 \times 10^4\,\mathrm{cm}^{-1}$.

As the energy of the laser beam was increased, the size of the microholes increased due to the Gaussian beam intensity distribution. Holes varied from 5 μm to 10 μm diameter at the exit as the laser energy was increased. The holes were drilled by placing the surface of the sample at the focal plane of the laser beam. It was observed that the holes at the entry of the sample were larger than the holes at the exit of the samples. Fine adjustments to the hole size were able to be made by controlling the number of pulses and changing the fluence. The taper of the through holes in the polymer is given by (Chen et al., 1995)

$$\theta = \frac{180}{\pi}\frac{1}{2}\frac{\phi_{\text{top}} - \phi_{\text{bottom}}}{t}, \qquad (2)$$

where t is the thickness of the sample and ϕ is the diameter of the hole. For this work, the taper is about 6.5 degrees.

Figure 6 shows the SEM micrographs of the holes drilled in PVA in the entry and exit for ultrafiltration

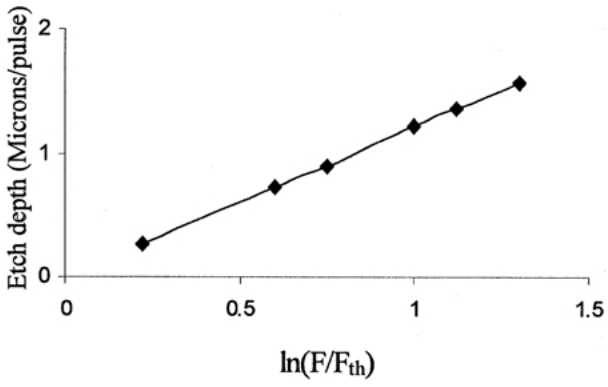

Fig. 5. *Relation between etching depths and logarithm of fluence for microholes at 266 nm wavelength.*

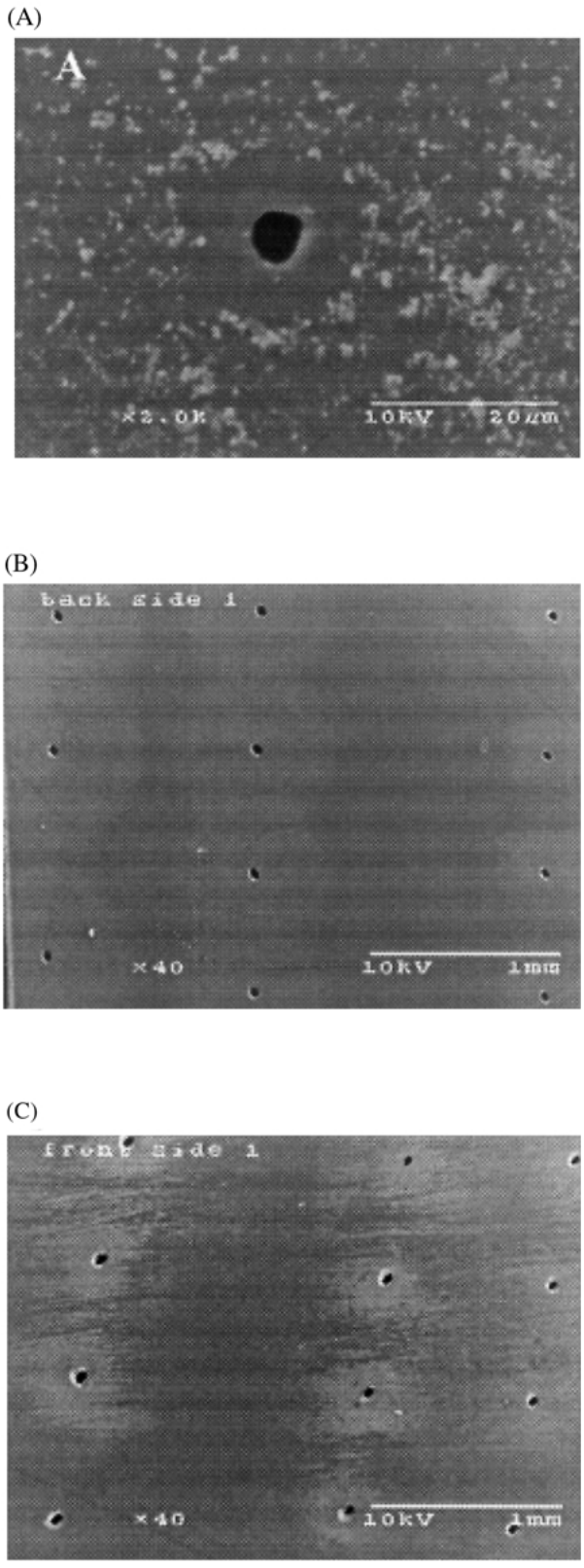

Fig. 6. *(A) Microhole at exit of the PVA at 266 nm wavelength, (B) View of ultrafiltration membrane at exit, and (C) View of ultrafiltration membrane at entry.*

membranes. The hole size measured around 5 μm at the exit. Micron-sized holes are highly reproducible by this laser direct etching technique.

It was observed that the polymer was ablated layer by layer upon multi-pulse irradiation. As the thickness of the sample was increased, more pulses were required to get a through hole, this is because the etch rate of the polymer is independent of the thickness of the polymer. At 266 nm wavelength, very few thermal damages were observed. The irregularities in the hole shape can be attributed to the spherical aberration and non-circularity of the laser beam, which can be improved by shaping the original laser beam and by better alignment of the optical components in the system.

4. Conclusions

Laser micromachining techniques for fabricating biodegradable micro-devices were demonstrated and reported. This work involves design and fabrication of two microdevices for potential applications in biomedical engineering. UV lasers were employed to etch microchannels and micro holes in biodegradable polymers. Microholes fabricated were 5–10 μm at the exit and the microchannels fabricated varied from 10–65 μm wide and 10–50 μm deep. The size of the features can be controled by changing laser parameters. Little thermal damage was observed in the laser etched micro-features.

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