Enhancement of Polymer Surface Adhesion by Laser Beam Irradiation for Microfluidic Chip Application: Formation of a Channel on a Modified Surface

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Polymethly methacrylate (PMMA) and polydimethlysiloxane (PDMS) surfaces were treated to improve adhesiveness by irradiation of a Nd:YAG pulse laser beam (λ=266 nm). A pulse laser beam was directed on a polymer surface in air, and the number of pulses was controlled by mobile velocity of a motorized stage. The laser treated surfaces were investigated using an optical microscope and a contact angle measuring instrument. It was thereby revealed that the contact angles were decreased in the laser treated surface. This in turn led to an increase of oxygen content and improved adhesiveness on the modified surface. With improved surface adhesion, a fluid channel could be formed on the laser treated surface region.

Keywords : Microfluidic chip, Surface modification, Nd:YAG laser, Contact angle, Hydrophilic

1. INTRODUCTION

Since the advent of silicon based microfluidic chips, various polymer based microfludic chips have been studied. A microfluidic chip, otherwise known as a Lab-on-a-Chip (LOC), has diverse micro channels that direct the flow of fluids and has seen application in the fields of biology and chemistry. These micro channels are made through micromachining. According to the embodiment of the LOC, extremely small quantities of fluids must be controlled.

In term of application to microfluidic chips, polymer materials, compared with traditional materials such as silicon and glass, offer economical efficiency, a simple manufacturing process, and wide material selectivity[1]. However, the hydrophilic property of polymers is universally lower than that of silicon or glass. To overcome this problem, various surface modification methods have been investigated. The purpose of surface modification is to improve the efficiency of the surface by making functional chemical combinations.

Surface enhancement of the hydrophilic property and adhesive strength can be achieved through surface modification[2,3]. Surface modification methods include chemical reaction, plasma treatment, mechanical abrasion, and laser beam irradiation[4-7]. Surface modification using a laser beam involves the application of simple equipment to directly irradiate a laser beam on the material surface in air.

In this study, polymer materials, polymethly methacrylate (PMMA) and polydimethlysiloxane (PDMS), which are widely used for LOC, were surface treated with a 4^{th} harmonic Nd:YAG pulse laser (λ=266 nm). After the laser treatment, the PMMA and PDMS surfaces were investigated using an optical microscope and a contact angle measuring instrument.

2. EXPERIMENT

This work, we treated PMMA and PDMS with a 4^{th} harmonic Nd:YAG pulse laser (λ=266 nm) for surface modification. The laser beam was arranged by a mirror and a focusing lens and irradiated on the sample surface. The sample was placed on an X-Y-Z motorized stage. Table 1 lists the experiment conditions to modify the surface. Figure 1 presents a schematic diagram of the

Table 1. Experiment conditions for PMMA and PDMS surface modification.

Experiment condition	Value
Laser power	0.1-0.7 W
Scan speed	30-5000 ㎛/s
Beam size(diameter)	5-8 mm
Number of Pulses	10-2700
Fluence	20-360 mJ/㎠

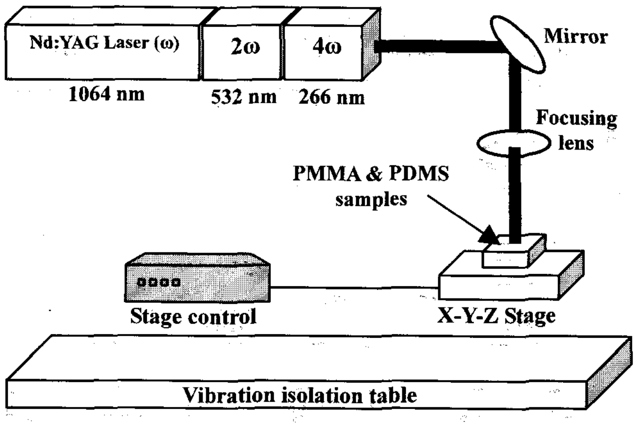

Fig. 1. Schematic diagram of laser treatment system.

laser modification system. The number of pulses directed on a given surface region was controlled by the mobile velocity of the stage. We attempted to find the threshold condition that marks the beginning point of surface etching.

The contact angles were measured after laser treatment in order to quantify surface modification rates. The surface energies (W) were calculated by the Young-Dupre equation using the measured contact angles (θ).

$$W = \gamma(1 + \cos\theta)\ [\mathrm{mN/m}] \qquad \gamma = 72.8\ [\mathrm{mN/m}] \qquad (1)$$

where γ is the surface energy of distilled water. As shown in Eq. 1, a decrease in the contact angle will occur as the surface energy is increased. In this work, 5 μl distilled water was dropped onto the laser treated polymer surface for measurement of the contact angle. Subsequently, the distilled water was lifted on modified surface using a syringe for conformation of the fluid channels after laser irradiation. This experimental process is schematically illustrated in Fig. 2.

3. RESULTS AND DISCUSSION

The beam fluence and the number of pulses were varied in order to find the threshold condition for the largest change of the contact angle. There was no surface damage below the threshold condition and surface etching began at the threshold. The threshold conditions for PMMA and PDMS are, respectively, 110 mJ/cm^2 and 115 mJ/cm^2, as shown in Table 2. These results are in agreement with the relationship between etching rate and beam fluence in polymer materials[8]. The relationship between beam fluence and etching rate is given in Eq. 2 and Fig. 3.

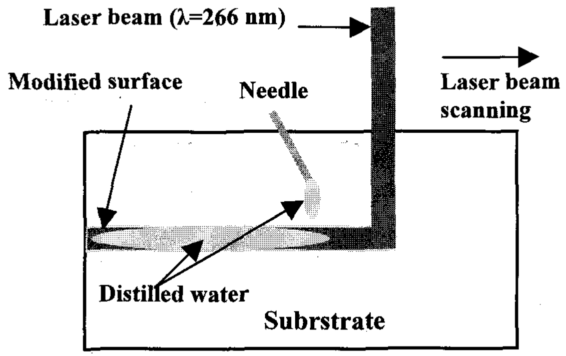

Fig. 2. Process of forming a fluid channel on the modified substrate.

Table 2. Threshold condition for the largest change of the surface modification of PMMA and PDMS.

Experiment condition	Value	
	PMMA	PDMS
Laser power	0.22 W	0.58 W
Scan speed	100 ㎛/s	250 ㎛/s
Beam size(diameter)	5 mm	8 mm
Number of Pulses	500	320
Fluence	110 mJ/㎠	115 mJ/㎠

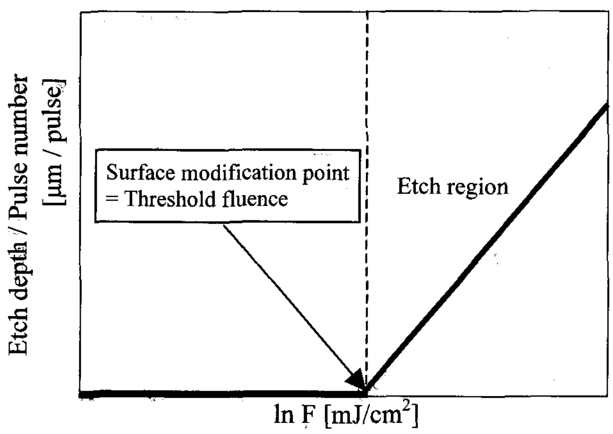

Fig. 3. Relationship between laser fluence and etching rate.

$$L_f = (1/\alpha)\ln(F/F_{th}) \qquad (2)$$

L_f: Etch depth per pulse
α: Absorptivity
F_{th}: Threshold fluence

The largest contact angle change of PMMA and PDMS was observed at the threshold condition. It has

Table 3. Contact angle and surface energy variation of the PMMA.

Experiment condition \ Measurement value		Minimum Contact angle(θ)	Surface energy
Untreated		75 ° (±1 °)	91.64 mJ/㎠
Laser treated	110 mJ/㎠ (Threshold)	59 ° (±1 °)	110.29 mJ/㎠
	150 mJ/㎠ (Etched surface)	65 ° (±1 °)	103.57 mJ/㎠

Table 4. Contact angle and surface energy variation of the PDMS.

Experiment condition \ Measurement value		Minimum Contact angle(θ)	Surface energy
Untreated		117 ° (±1 °)	39.74 mJ/㎠
Laser treated	115 mJ/㎠ (Threshold)	101 ° (±1 °)	58.91 mJ/㎠
	128 mJ/㎠ (Etched surface)	105 ° (±1 °)	53.96 mJ/㎠

been reported that the contact angle is inversely proportional to the surface oxygen contents[9-11]. Therefore, photo oxidation, i.e., the increase of surface oxygen content, occurred maximally at the threshold condition. The data shown in Table 3 and Table 4 show that the laser treated surface contact angle at the threshold condition was lower than the contact angle beyond the threshold condition. Figure 4 and Fig. 5 show optical microscope surface photographs of (a) untreated, (b) threshold, and (c) etching conditions for PMMA and PDMS, respectively. It is thought that etching takes place instead of photo oxidation if laser energy in excess of the threshold is irradiated[12]. The etched surfaces can be observed in Fig. 4c and Fig. 5c.

The modification rate is defined as the rate of change of the treated surface contact angle for the untreated surface contact angle. The maximum modification rate of PMMA and PDMS at the threshold is 21.3 % and 14.0 %, respectively, as given in Table 3 and Table 4. Therefore, the laser treated PMMA surface has higher modification efficiency than the PDMS surface. It is considered that PMMA is more effective than PDMS as a laser surface modified LOC substrate. A fluid channel was formed on the enhanced PMMA surface. The width of the fluid channel is about 3 mm, as shown in Fig. 6b. However, the fluid channel was not formed on the untreated surface, as shown in Fig 6a. This result reflects the improvement of wettability and adhesion on the material surface irradiated by a focused a laser beam.

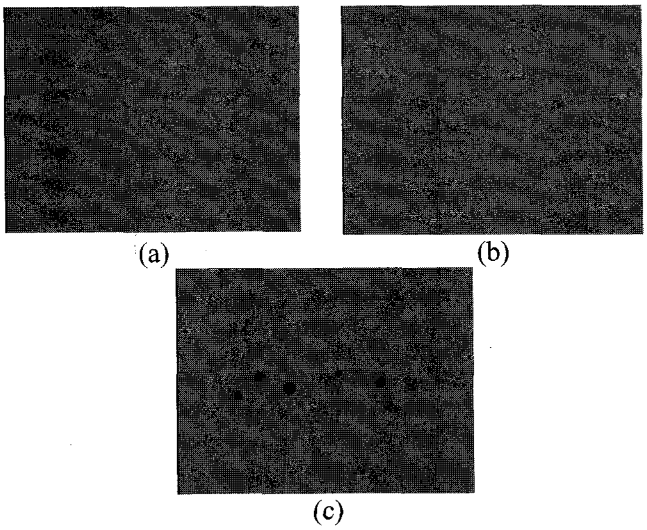

Fig. 4. Optical microscope surface images of PMMA: (a) untreated (b) laser treated at 110 mJ/㎠ (threshold) (c) laser treated at 150 mJ/㎠ (etched surface).

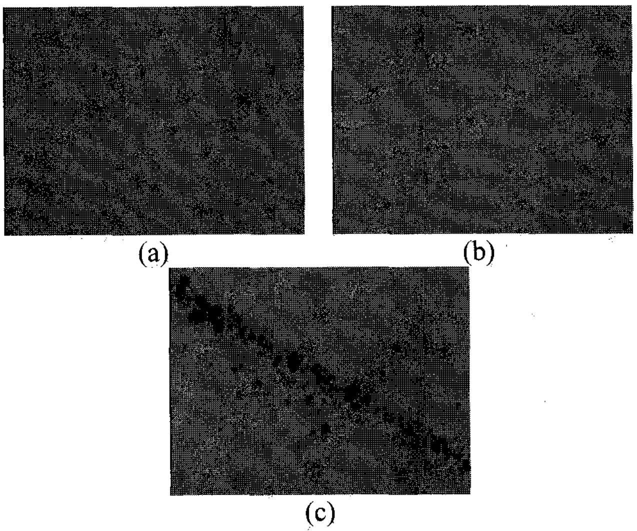

Fig. 5. Optical microscope surface images of PDMS: (a) untreated (b) laser treated at 115 mJ/㎠ (threshold) (c) laser treated at 128 mJ/㎠ (etched surface).

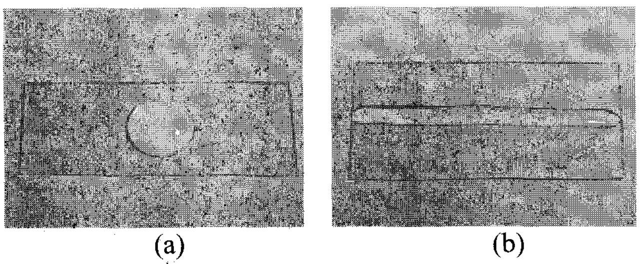

Fig. 6. Images of PMMA surface: (a) untreated (b) laser treated at 110 mJ/㎠ (threshold).

4. CONCLUSION

Polymer surfaces were modified by a 4th harmonic Nd:YAG pulse laser (λ=266 nm) for enhancement of surface adhesion. Through experiments, the authors determined a threshold condition at which surface etching commenced and maximal modification occurred. The maximum modification rate of PMMA is 21.3 %, which is 7.3 % higher than that of PDMS. The modified surface energy of PMMA is also higher than that of PDMS. Therefore, it is concluded that PMMA has higher modification efficiency than PDMS by laser treatment. It is thought that PMMA is more effective than PDMS in term of application as a LOC material. Lastly, a fluid channel was successfully formed on the PMMA surface, indicating that focused laser beam modification of a polymer surface is a feasible approach for microfluidic chip applications.

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