Pulsed Laser Drilling of Engineering Plastic Films to Fabricate Through-Hole Membranes for Print-and-Imprint Method

Takahiro Nakamura¹, Kento Seki¹, Kazuro Nagase², and Masaru Nakagawa^{1*}

¹ Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University,

2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

² MINO GROUP Co., Ltd., 8-2 Kamita, Minami-cho, Gujo, Gifu 501-4101, Japan

* Corresponding author: masaru.nakagawa.c5@tohoku.ac.jp

Laser drilling of engineering plastic films was performed using a picosecond pulsed laser at different repetition rates for the application of through-hole membranes to laser-drilled screen printing. Four engineering plastic films of polyimide (PI), poly(ethylene terephthalate) (PET), poly(phenylene sulfide) (PPS), and poly(ether ether ketone) (PEEK) were investigated. Frustum-shaped through holes were formed with high reproducibility by laser drilling at a repetition rate of 10 kHz. Higher repetition rates induced the formation of heat affected zone around the edge of the through holes in the case of engineering plastic films with their low melting point. The mean diameters of through holes formed on the film surfaces of both laser entry and exit sides at the identical repetition rate increased in the order of PEEK $\approx$ PET < PI < PPS, which had a relationship with the optical absorption properties at the wavelength of the laser pulses. It was suggested that the PI film was appropriate to a laser-drilled through-hole membrane in terms of the shape of through holes in addition to its chemical and thermal stabilities.

Key words: pulsed laser drilling, engineering plastic film, picosecond laser, through-hole membrane

1. INTRODUCTION

Laser micro-processing such as etching, drilling, and cutting of materials has been widely applied in a variety of industrial fields to date. As the laser is developed, the specific characteristics of wavelength, energy, pulse duration and so on become easily available. In particular, the progress of short pulse lasers enables the fine processing of metals [1,2], ceramics [3,4], semiconductors [5,6], and composites [7,8] with minimal heat affected zone (HAZ) and less debris around laser-irradiated areas. Transparent materials without absorption at the wavelength of the incident laser can also be processed through multiphoton absorption due to high peak power at the focal spot [9-11].

Laser processing of engineering plastics has been intensively studied using short pulse lasers since first demonstration of photoetching of engineering plastics by an excimer laser in 1983 [12,13]. Ito et al. studied photo-ablative behavior of polyimide by nanosecond lasers with different wavelengths, demonstrating that the high absorption coefficient at a short wavelength of a laser beam makes high-quality holes without thermal damage [14]. Kumagai et al. investigated laser ablation of polymer films of polytetrafluoroethylene, tetrafluoroethylene-hexafluoropropylene copolymer, and polyimide (PI) through multiphoton absorption using a femtosecond high-peak-power Ti:sapphire laser at 798 nm [15]. High-quality laser processing of engineering plastics of PI [16-18], poly(methyl methacrylate) [19-21], and a conductive polymer of poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) [22] has been demonstrated. However,

practical applications of laser-processed engineering plastics are scarce up to date.

We reported the print-and-imprint method comprising laser-drilled screen printing and nanoimprinting [23]. A PI through-hole membrane was used as a screen printing mask, which was prepared by laser drilling using a picosecond pulsed laser in consideration of its advantages of high output power, stable operation, and low running cost rather than other short pulse lasers. In laser-drilled screen printing, droplets of high-viscosity UV-curable liquid with a viscosity of 11,000 mPa s can be placed site-selectively on a substrate surface. The mean volume of a droplet was 0.12 pL which is smaller than that dispensed by inkjet printing suitable for low-viscosity liquids in the range of 5–20 mPa s. Therefore, laser-drilled screen printing has a potential for placement of high-viscosity materials on substrate surfaces. Here, we investigated laser drilling of four engineering plastic films using a picosecond pulsed laser for the application of through-hole membranes to laser-drilled screen printing. The mechanism for forming through holes into the engineering plastic films at different repetition rates was discussed in terms of their optical absorption properties at the wavelength of the incident laser beam and their thermal properties.

2. EXPERIMENT

Laser drilling was performed using laser pulses emitted by second-harmonic generation of a mode-locked Nd:YAG picosecond pulsed laser (Coherent LFP-20TG). The central wavelength (λ) was 532 nm, and the pulse width was 12.5 ps.

Fig. 1 Laser drilling system for fabrication of through-hole membranes of engineering plastic films.

The laser pulses passed through an optical system (assembled by Sigmakoki) as illustrated in Fig. 1. In the laser drilling system, a laser beam was collimated through a beam expander, and the laser pulse energy was tuned using a variable attenuator. The minimum laser pulse energy of 1.2 μJ through the attenuator was used for laser drilling to avoid the formation of HAZ around through holes. The repetition rate of laser pulses was tuned in the range of 0.25–50 kHz to control the diameters of through holes. The laser pulses were focused onto a film surface of the laser entry side through a focusing lens with a focal length of 40.2 mm and a numerical aperture of 0.34. The exposure period was set at 0.1 s using a high-speed mechanical shutter inserted in the laser axis. An engineering plastic film was fixed to a computer-controlled linear motor stage with a position accuracy of 0.1 μm (Sigma Tech BIOS-415S) which was moved stepwise during laser irradiation. Laser pulses were exposed onto a film surface at ten-by-ten positions with a pitch of 60 μm . Laser drilling process was monitored with a charge-coupled-device (CCD) camera (Sigmakoki SK-N63SCJ-C). The hole shapes of both laser entry and exit sides formed on the film surfaces were observed using a digital microscope (Keyence VHX-200 or VHX-1000). The mean diameters of holes formed on the film surfaces were analyzed with software (Mitani WinRoof). Four engineering plastic films of 12.5 μm -thick PI (Du Pont-Toray Kapton50H/V), 12.0 μm -thick poly(ethylene terephthalate) (PET; Toray Lumirror S10), 9.0 μm -thick poly(phenylene sulfide) (PPS; Toray Trelina3030), and 12.0 μm -thick poly(ether ether ketone) (PEEK; Kurabo EXPEEK) were used in this study. The characteristics of thermal and mechanical properties are summarized in Table I. UV-visible transmission spectra were taken using a spectrophotometer (Shimadzu Multispec-1500). Fourier-transformed scanning electron microscope (FE-SEM) observation was carried out using a High-Technologies S-4800).

Table I Characteristics of engineering plastic films used for laser drilling.

film	d (μm)	m.p. ($^{\circ}\text{C}$)	T_d ($^{\circ}\text{C}$)	tension st. (MPa)
PI	12.5	-	> 500	325 – 355
PET	12.0	260	240	48 – 73
PPS	9.0	280	260 – 270	66 – 86
PEEK	12.0	343	> 250	71 – 103

t = film thickness, m.p. = melting point, T_d = degradation temperature, tension st. = tension strength.

3. RESULTS AND DISCUSSION

Figure 2 shows UV-visible transmission spectra of (a) PI, (b) PET, (c) PPS and (d) PEEK films in the measurement range of 200–800 nm. The dotted line indicated vertically at 532 nm means the wavelength of the exposed laser beam. Oscillation in the spectra in the long wavelength range was due to optical interference with probing light. The transmittance values at 532 nm were 65.2 % for PI, 81.9 % for PET, 46.1 % for PPS, and 84.1 % for PEEK. The film transparency was low in order of PPS < PI < PET $\approx$ PEEK.

Fig. 2 UV-visible transmission spectra of (a) PI, (b) PET, (c) PPS, and (d) PEEK films.

Figure 3 shows optical microscope images of through holes formed on laser exit surfaces of PI [Fig. 3(a)], PET [Fig. 3(b)], PPS [Fig. 3(c)], and PEEK [Fig. 3(d)] after laser irradiation for 0.1 s with different repetition rates in the range of 0.25–50 kHz. Each magnification image in the inset corresponds to a hole which is located at the upper right corner of 100 holes in the figure. As shown in Fig. 3(a), it was found that through holes were formed on a PI film surface of the laser exit side at repetition rates of 0.5–50 kHz. This suggested that the formation of through holes in the 12.5 μm -thick PI film had a threshold of 0.5 kHz. In contrast, through holes were formed in the PET, PPS and PEEK films by laser irradiation at a small repetition rate of 0.25 kHz. The hole diameters observed for the laser exit side increased with increasing the repetition rates. However, the morphological deformation around through holes was observed for the through holes formed on PET, PPS and PEEK film surfaces of the laser exit side by laser irradiation at a repetition rate of 50 kHz. The deformation of hole shapes was not observed for the PI film at the same repetition rate. PET, PPS, and PEEK exhibit a melting point (m.p.) of 260, 280, or 343 $^{\circ}\text{C}$, respectively, while PI hardly shows an obvious melting point before its thermal degradation temperature of >500 $^{\circ}\text{C}$. It was anticipated that high-repetition-rate laser exposure caused thermally induced deformation around areas exposed to laser pulses owing to the presence of melting points. Such thermally induced deformation is called as HAZ [24]. In consideration of using a through-hole membrane as a screen printing mask, the thermally induced deformation around through holes is

afraid of causing the volumes of individual droplets to vary dependently on the hole shapes.

(a) polyimide (PI)

(b) polyethylene terephthalate (PET)

(c) polyphenylene sulfide (PPS)

(d) polyether ether ketone (PEEK)

Fig. 3 Optical microscope images of holes formed on (a) PI, (b) PET, (c) PPS, and (d) PEEK film surfaces of the laser-exit side.

The mean diameters (d_{entry}) formed on the laser-entry film surfaces, ones (d_{exit}) formed on the laser-exit film surfaces, and the difference values [$\Delta d = (d_{\text{entry}} - d_{\text{exit}})$] by laser irradiation with different repetition rates are plotted as a function of repetition rate of no smaller than 1 kHz in Fig. 4. The respective values were determined by optical microscope observation of 100 holes except for holes affected by HAZ. In all the cases, the d_{entry} values were larger than the d_{exit} values, indicating that the through-holes had a frustum-shaped structure. The difference values (Δd) observed for PI had a trend obviously different from those observed for the other

engineering films. In the case of PI, the difference value of $\Delta d = 8.7 \mu\text{m}$ at 1 kHz decreased to approximately $\Delta d = 6 \mu\text{m}$ at increased repetition rates. This indicated that laser drilling of PI occurred from the PI surface of the laser entry side. The d_{entry} and d_{exit} values were almost constant at repetition rates between 10 and 25 kHz. This suggested that laser ablation to cause laser drilling of PI almost finished at 10 kHz for a constant exposure period of 0.1 s.

Fig. 4 Changes in d_{entry} , d_{exit} , and Δd as a function of repetition rate in the case of (a) PI, (b) PET, (c) PPS, and (d) PEEK films.

To the contrary, the difference values (Δd) of approximately $5 \mu\text{m}$ at 1 kHz increased with increasing repetition rates in the case of PET, PPS, and PEEK. The mean diameters of d_{entry} and d_{exit} observed for PPS and PEEK became almost constant over 10 kHz. This indicated that the repetition rate of 0.25 kHz allowed laser drilling, and the laser drilling of PPS and PEEK finished at 10 kHz. There was a characteristic of d_{entry} and d_{exit} observed for PET. Both of the mean diameters increased with increasing from 1 kHz to 2.5 kHz, were maintained at an almost constant value until 10 kHz, and then increased again over 10 kHz. This suggested that laser drilling of PET almost finished at 10 kHz and excess laser pulses increased HAZ around through holes, resulting in larger d_{entry} and d_{exit} values owing to its low melting point. Consequently, we demonstrated that through holes could be fabricated in the four engineering plastic films by laser drilling with 10 kHz for 0.1 s. The d_{exit} values were $9.3 \mu\text{m}$ for PI, $9.0 \mu\text{m}$ for PET, $11.7 \mu\text{m}$ for PPS, and $9.0 \mu\text{m}$, which increased in the order of $\text{PEEK} \approx \text{PET} < \text{PI} < \text{PPS}$. The tendency was consistent with the low transmittance at a laser wavelength of 532 nm as shown in Fig. 2. It was concluded that through holes with larger diameters were formed in the film with high absorption property at the laser wavelength. The PI films were appropriate to through-hole membranes fabricated by laser drilling because of the controllability of the hole diameters and the thermal stability in addition to the chemical stability.

Surface morphologies of through holes laser-drilled on PI film surfaces with different repetition rates were observed using a FE-SEM. As shown in Fig. 5, debris around through holes after laser drilling was removed by

a cleaning process of washing PI through-hole membranes in surfactant-containing water under ultrasonic wave and rinsing with deionized water. It was confirmed that the through holes had a frustum-shape. The hole shapes were almost independent of repetition rate in the range of 10–50 kHz.

Fig. 5 FE-SEM images of through holes laser-drilled on PI surfaces of the laser entry side with repetition rates of (a) 1, (b) 5, (c) 10, and (d) 50 kHz.

4. CONCLUSION

We investigated laser drilling of PI, PET, PPS, and PEEK films using a picosecond pulsed laser emitted at 532 nm. Through holes could be fabricated with high reproducibility by laser drilling at a repetition rate of 10 kHz for 0.1 s. The diameters of the holes formed on the film surfaces of laser entry and exit sides increased in the order of PEEK $\approx$ PET < PI < PPS. The order was consistent with that of the absorption property at the laser wavelength. Namely, the high absorption property caused the hole diameter of the laser exit side to be enlarged. Among the four engineering plastics, the PI film was suitable for the fabrication of through-hole membranes owing to the controllability of the hole diameters and the chemical and thermal stability. We concluded that the PI through-hole membranes will be sufficiently available for laser-drilled screen printing to place liquid droplets of UV-curable resins site-selectively onto a substrate surface for print-and-imprint methods.

References

- [1] C. Momma, B. N. Chichkov, S. Nolte, F. Alvensleben, A. Tünnermann, H. Welling, and B. Wellegehausen, *Optics Comm.*, **129**, 134–142 (1996).
- [2] K.-H. Leitz, B. Redlingshöfer, Y. Reg, A. Otto, and M. Schmidt, *Phys. Procedia*, **12**, 230–238 (2011).
- [3] S. H. Kim, I.-B. Sohn, and S. Jeong, *Appl. Surf. Sci.*, **255**, 9717–9720 (2009).
- [4] N. Bärsch, A. Gatti, and S. Barcikowski, *JLMN-J. Laser Micro/Nanoeng.*, **4**, 66–70 (2009).
- [5] J. Bonse, S. Baudach, J. Krüger, W. Kautek, and M. Lenzner, *Appl. Phys. A*, **74**, 19–25 (2002).
- [6] S. Döring, T. Ullsperger, F. Heisler, S. Richter, A. Tünnermann, and S. Nolte, *Phys. Procedia*, **41**, 431–440 (2013).
- [7] R. Weber, C. Freitag, T. V. Kononenko, M. Hafner, V. Onuseit, P. Berger, and T. Graf, *Phys. Procedia*, **39**, 137–146 (2012).

- [8] M. Fujita, T. Sonekawa, and N. Miyanaga, *Phys. Procedia*, **41**, 636–639 (2013).
- [9] S. Butkus, D. Paipulas, R. Sirutkaitis, E. Gaižauskas, and V. Sirutkaitis, *JLMN-J. Laser Micro/Nanoeng.*, **9**, 213–220 (2014).
- [10] K. L. Włodarczyk, A. Brunton, P. Rumsby, and E. P. Hand, *Opt. Laser. Eng.*, **78**, 64–74 (2016).
- [11] T. Alqurashi, Y. Montelongo, P. Penchev, A. K. Yetisen, S. Dimov, and H. Butt, *Nanoscale*, **9**, 13808–13819 (2017).
- [12] Y. Kawakami, K. Toyoda, and S. Namba, *Appl. Phys. Lett.*, **40**, 374–375 (1982).
- [13] R. Srinivasan and V. M.-Banton, *Appl. Phys. Lett.*, **41**, 576–578 (1982).
- [14] K. Ito, M. Moriyasu, and H. Kawasumi, *J. Photopolym. Sci. Technol.*, **6**, 393–400 (1993).
- [15] H. Kumagai, K. Midorikawa, K. Toyoda, S. Nakamura, T. Okamoto, and M. Obara, *Appl. Phys. Lett.*, **65**, 1850–1852 (1994).
- [16] B. Haba and Y. Morishige, *Appl. Phys. Lett.*, **66**, 3591–3593 (1995).
- [17] K. C. Yung and D. W. Zeng, *Surf. Coat. Technol.*, **145**, 186–193 (2001).
- [18] V. N. Tokarev, J. Lopez, S. Lazare, and F. Weibuch, *Appl. Phys. A*, **76**, 385–396 (2003).
- [19] S. Baudach, J. Bonse, J. Krüger, and W. Kautek, *Appl. Surf. Sci.*, **154–155**, 555–560 (2000).
- [20] B. Xia, L. Jiang, X. Li, X. Yan, W. Zhao, and Y. Lu, *Appl. Phys. A*, **119**, 61–68 (2015).
- [21] Y. Yu, L. Jiang, Q. Cao, B. Xia, Q. Wang, and Y. Lu, *Opt. Express*, **23**, 32728–32735 (2015).
- [22] S. Xiao, S. A. Fernandes, C. Esen, and A. Ostendorf, *J. Laser Micro/Nanoeng.*, **6**, 250–254 (2011).
- [23] T. Nakamura, K. Seki, K. Nagase, and M. Nakagawa, *J. Vac. Sci. Technol.*, **35**, 06G301(1–8) (2017).
- [24] F. Schneider, N. Wolf, and D. Petring, *Physics Procedia*, **41**, 415–420 (2013).

(Received April 28, 2018; Accepted August 24, 2018;
Published Online October 1, 2018)