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# Fabrication of Micro-Structured Surface of Plants-Derived Polyamide using Femtosecond Laser and Their Frictional Properties

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**Abstract.** For the purpose of developing the new polymeric tribomaterials using biopolymer, the fabrication of microstructured surfaces of plants-derived polyamide (PA) using femtosecond laser and their frictional properties were investigated. In this study, the effect of processing parameter such as laser power, laser speed and pitch distance on the fabrication of micro-structured surfaces of polyamide 66 (PA66) and plants-derived polyamide 1010 (PA1010) was investigated experimentally, and their frictional properties and wettability were evaluated. Polyamides (PA1010 and PA66) were extruded by a twin screw extruder and injection-molded to 30mm x 30mm x 3mm sheet. The micro-structured surfaces on the polyamides were fabricated by femtosecond laser. The micro-structured surfaces on the polyamides by laser fabrication were observed by laser microscope and scanning electron microscope (SEM). Frictional properties were measured by a ball on plate reciprocating type sliding wear tester under lubrication conditions. It was found that the surface microchannels are able to be fabricated by the femtosecond laser and have a good effect for the improvement of the frictional properties and wettability of PA66 and plants-derived PA1010. Laser power influences strongly on the microchannels size, wettability and frictional properties. This may be attributed that the micro-structured surface plays an important role in the key components for the polymeric tribomaterials.

# INTRODUCTION

Surface texturing technology has been widely used to improve the functionality of materials surface wettability and frictional characteristics in recent years<sup>1)</sup>. This is because the micro-structured surface such as regularly microchannels can contribute to friction reduction at sliding contact interfaces and can provide micro-reservoirs to enhance lubricant retention or micro-traps to capture wear debris<sup>2)-4)</sup>. Laser surface texturing (LST) has been a great attention due to its versatility and precision for surface texturing technique with respect to metallic materials utilizing laser with a wide range of wave lengths and pulse energies<sup>5), 6)</sup>. Especially, in this field, the conduction heat transfer in materials treated under short time scales in the ablation process with femtosecond laser pulses is negligible compared with that generated using picosecond and nanosecond pulse lasers<sup>7)</sup>. Therefore, femtosecond lasers enhance precision and pure laser processing in surface texturing. Moreover, most tribological studies of surface texturing have focused on the modification of ceramics and metallic materials, since they are the primary engineering materials. On the other hand, the polymeric materials have replaced metals due to their superior performance, which is high specific strength, ease of processability, and low cost. Therefore, applications of a surface texturing technique for polymeric materials should be investigated. In our previous works, we investigated the fabrication of micro-structured surface of polymeric materials such as polytetrafluoroethylene (PTFE) and



polyamide 11 elastomer (PA11E) and their frictional properties<sup>8)-10)</sup>. For the purpose of developing the new tribomaterials, the fabrication of micro-structured surfaces of polyamide (PA) using femtosecond laser and their frictional properties were investigated. However, most polymeric materials are derived from petroleum supply resources, therefore there is a demand to replace them to biopolymer such as plants-derived polymer because of the problems of uncertainly of the petroleum supply and global warming<sup>11)</sup>. For the purpose of developing the new polymeric tribomaterials using biopolymer, the fabrication of micro-structured surfaces of plants-derived polyamide (PA) using femtosecond laser and their frictional properties were investigated. In this study, the effect of processing parameter such as laser power, laser speed and pitch distance on the fabrication of micro-structured surfaces of polyamide 66 (PA66) and plants-derived polyamide 1010 (PA1010) was investigated experimentally, and their frictional properties and wettability were evaluated.

# **EXPERIMENTAL**

The materials used in this study were two types of polyamide: plants-derived Polyamide 1010 (PA1010, Vestamid Terra DS16, DaicelEvonic Ltd., Japan) and petroleum-derived polyamide 66 (PA66, Zytel 101L, Du Pont Ltd., Japan). PA1010 was made from sebacic acid and decamethylendiamine, which are obtained from plantsderived castor oil. PA1010 and PA66 were dried in vacuum oven at 80°C for 12h and 90°C for 12h, respectively. Subsequently PA1010 and PA66 were melt kneaded by a twin screw extruder (TEX-30, Japan Steel Works, Ltd., Japan) and injection molded (NS20-A, Nissei Plastic Industrial, Japan) to 30mm x 30mm x 3mm specimens. The molding conditions of PA1010 were kneading and cylinder temperatures of 220°C and mold (cavity) temperature of 30°C, and those of PA66 were kneading and cylinder temperatures of 270°C and mold (cavity) temperature of 80°C, respectively. To keep the drying conditions of specimens for all measurements, they were kept in accordance with JIS K 6920-2 for at least 24h at 23°C in desiccators after injection molding. Surface microchannels on behalf of the micro-structured surface on PA were fabricated by femtosecond laser (IFRIT, Cyber laser Inc., Japan). The surface microchannels area in this study was a rectangle region of 3mm x 25mm. Femtosecond laser was performed to generate linearly polarized laser pulses at a wave length of 800nm, and with pulse duration of 190fs. The processing parameters in this study were three: the first is laser power (0.2-1W), the second is laser speed (200-1200mm/min) and the third is pitch distance of microchannels (20-100µm). These detailed processing parameters were listed in Table 1. The surface microchannels on the polyamides by laser fabrication were observed by laser microscope (VK-X200, Keyence Co., Japan) and scanning electron microscope (SEM, JSM6360LA, Jeol Ltd., Japan). Wettability of the polymeric materials with surface microchannels was measured by contact angle gauge (Phoenix-300, Meiwafosis Co., Ltd., Japan), and the drop volume of deionized water was 5 µl. Frictional properties were measured by a ball on plate reciprocating type sliding wear tester (HEIDON Type38, Shinto Scientific Co., Ltd., Japan) under oil lubrication sliding conditions, at room temperature. The test conditions were selected as sliding speed of 10 mm/s, sliding distance of 300mm and normal load of 0.2N. The carbon-chromium bearing steel (SUJ2) ball (\$\phi 2.5mm\$) was used as counterpart and the silicone oil (KF-96-100cs, Shin-Etsu Chemical Co., Ltd.) was used as oil lubricant.

 Laser power, (W)
 0.2, 0.4, 0.6, 0.8, 1.0

 Laser speed, (mm/min)
 200, 400, 600, 800, 1000, 1200

 Pitch distance, (μm)
 20, 30, 40, 50, 100

 Focal length, (mm)
 50

 Pulse duration, (fs)
 190

 Wave length, (nm)
 800

**TABLE 1.** The processing parameter used in this study

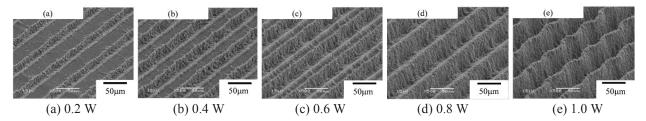
### RESULTS AND DISCUSSION

First, the effect of laser power on the fabrication of micro-structured surface of polyamides is discussed. Fig. 1 and Fig. 2 show the image of SEM photographs of microchannels on the PA66 and plants-derived PA1010 at the laser speed of 400mm/min and various laser powers, respectively. The microchannel width  $W_M$  and microchannel depth  $H_M$  of both polyamides increase gradually with increasing laser power, and thus the width of un-fabricated surface (no laser irradiation area) decreases. These results are the same tendencies as the microchannels on the

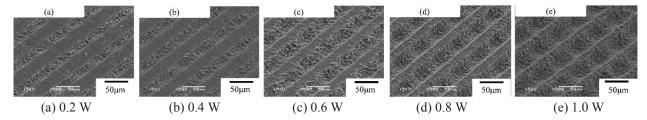


silicone by Crawford et al.<sup>12)</sup> and the PTFE by Naruse et al.<sup>8)</sup>. The size of microchannels is closely related to the energy density, which is the multiplication of laser power and laser speed. On the other hand,  $W_M$  and  $H_M$  of plants-derived PA1010 are bigger than those of PA66. These behaviors may be due to the difference of laser resistance of each polymeric material.

To more clarify the influence of laser power on the microchannel sizes of various polyamides, these sizes were measured by laser microscope. Fig. 3(a) shows the influence of laser powers on the microchannel width  $W_M$  of PA66 and plants-derived PA1010 at the laser speed of 400mm/min.  $W_M$  increases linearly with increasing the laser power, and  $W_M$  of plants-derived PA1010 is bigger than that of PA66. Fig. 3(b) shows the influence of laser power on the microchannel depth  $H_M$  of PA66 and plants-derived PA1010 at the same condition.  $H_M$  shows the same tendencies as  $W_M$ . Especially  $H_M$  of plants-derived PA1010 is about three times bigger than that of PA66. Fig. 3(c) shows the influence of laser power on the aspect ratio  $H_M/W_M$  of microchannels of PA66 and plants-derived PA1010 at the same conditions. Here, this aspect ratio of microchannels given by microchannel depth  $H_M$  divided by microchannel width  $W_M$ .  $H_M/W_M$  increases with increasing laser power, and  $H_M/W_M$  of plants-derived PA1010 is 2.5 times or bigger than that of PA66.



**FIGURE 1.** SEM photographs of microchannels on the plants-derived PA1010 at the laser speed of 400mm/min and various laser powers (x500)



**FIGURE 2.** SEM photographs of microchannels on the PA66 at the laser speed of 400mm/min and various laser powers (x500)

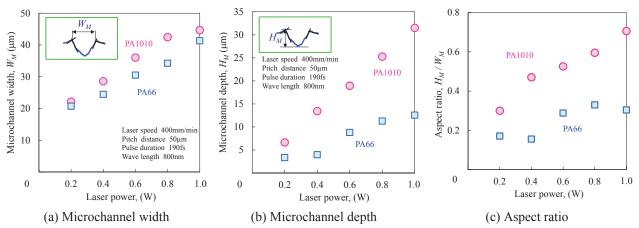


FIGURE 3. Influence of laser power on the microchannel sizes of various polyamides

Next, the effect of laser power on the wettability of various polyamides with microchannels is discussed. Fig. 4 shows the influence of laser power on the contact angle of PA66 and plants-derived PA1010. The contact angle  $\theta$  of both PA66 and plants-derived PA1010 decreases with increasing the laser power. Thus, the surface of polyamides with microchannels becomes more hydrophilic than the non-textured surfaces. According to the report of Ma et al., in the case of the Wenzel model, the liquid is assumed to be completely wetting the mutual interface, which makes the hydrophobic surface more hydrophobic one, meanwhile the hydrophilic surface more hydrophilic one<sup>13</sup>. On the other hand,  $\theta$  of plants-derived PA1010 is larger than that of PA66. This may be due to the difference of the value of microchannel aspect ratio  $H_M/W_M$ . This phenomenon is explained by Cassie-Baxter model, in which the air can be trapped on the rough surface under the liquid<sup>14</sup>. The micro-structured patterns having periodic structure of micron order and larger aspect ratio such as microchannels in this study trap the air in the bottom of microchannels, therefore the contact angle becomes larger and hydrophobic. From Fig. 2(c) it can be stated that the wettability of plants-derived PA1010 become more hydrophobic than that of PA66.

Finally, the effect of laser power on the frictional properties of PA66 and plants-derived PA1010 with microchannels by constant normal load and sliding speed testing using a ball on plate reciprocating type sliding wear tester under oil lubrication is discussed. Fig. 5 shows the relationship between the frictional coefficient  $\mu$  and laser power of PA66 and plants-derived PA1010.  $\mu$  of the surface textured with microchannels of both PA66 and plants-derived PA1010 is higher than that of non-textured surface of polyamides. This tendency may be due to the difference of surface roughness of un-fabricated surface, which is no laser irradiation area between the fabricated microchannel and one, and that of non-textured surface. However, the reason of the no difference between PA66 and plants-derived PA1010 is unknown at this time. The effect of other processing parameter such as laser speed, laser spot size, focal length and distance on the microchannel size, wettability and frictional properties will be reported at the Conference presentation.

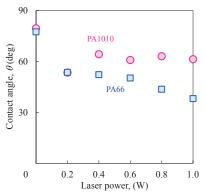
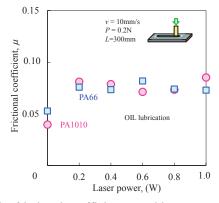


FIGURE 4. Influence of laser power on the contact angle of PA66 and plants-derived PA1010



**FIGURE 5.** Relationship between the frictional coefficient  $\mu$  and laser power of PA66 and plants-derived PA1010



### **CONCLUSION**

For the purpose of developing the new polymeric tribomaterials using biopolymer, the fabrication of micro-structured surface of plants-derived polyamide (PA) using femtosecond laser and their frictional properties were investigated. In this study, the effect of processing parameter such as laser power, laser speed and pitch distance on the fabrication of micro-structured surface of polyamide 66 (PA66) and plants-derived polyamide 1010 (PA1010) were investigated experimentally, and their frictional properties and wettability were evaluated. It was found that the surface microchannels are able to be fabricated by the femtosecond laser and have a good effect for the improvement of the frictional properties and wettability of PA66 and plants-derived PA1010. The effect of laser power influences strongly on the microchannel size, wettability and frictional properties. This may be attributed that the micro-structured surface plays an important role in the key components for polymeric tribomaterials.

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