Fabrication of Cotton-like Superhydrophobic Surface on Teflon Using a Pulsed Ultraviolet Laser

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Cotton-like micro structures were selectively fabricated on Teflon (Polytetrafluoroethylene) surface by irradiating focused fourth harmonic of Nd:YAG lasers two dimensionally, which were found to have superhydrophobic property. The wavelength, pulse duration, focusing diameter and the energy of the laser were 266 nm, 10 ns, about 2 μm and about 0.1 mJ, respectively. The contact angle of 140 degrees was obtained for the machining pitches of 10 μm, while that for unfabricated surface was about 90 degrees. The method described is purely physical process, therefore the superhydrohobic surface obtained is considered to keep various valuable chemical characteristics of Teflon.

DOI:10.2961/jlmn.2010.02.0007
Keywords: Teflon, Polytetrafluoroethylene, superhydrohobic surface, ultraviolet laser

1. Introduction

Teflon (Polytetrafluoroethylene) has various chemical and physical features, such as chemical stability, electric insulation property, nonadherent property, low friction property, high water repellency and so on. Teflon is transparent for wide range of the electromagnetic radiation. Therefore, it is widely used in various engineering and scientific fields, and considered to be one of the most important plastic materials. The hardness of Teflon is not so high as the standard plastics, and it locates between the plastics and the rubbers, which is a very few disadvantages of Teflon.

Pulsed ultraviolet laser, such as KrF Excimer lasers (248 nm) and the fourth harmonic of Nd:YAG lasers (266nm), have been used for micro fabrications since early 1980s [1-5]. These lasers have been also used for creating special surface properties of metals and polymers, such as the increasing in adhesiveness of Teflon by the photo-chemical processing assisted by an Excimer laser irradiation [6-8]. They are also used for the micro fabrication in the field of semiconductor processing [9].

In the nature, micro structures on the lotus leave are known to cause strong water repellency [10]. Artificially, various methods have been reported for the generation of the water repellent surfaces [11].

In this paper, it is reported that the cotton like micro structures were selectively fabricated on the surface of Teflon using a fourth harmonic of Nd:YAG laser, which was found to have high water repellent property. The wavelength, pulse duration, focusing diameter and the energy were 266 nm, 10 ns, about 2 μm and about 0.1 mJ, respectively. The laser was irradiated with the pitches of 10 μm～40 μm on the surface two-dimensionally. The maximum contact angle of 140 degrees was obtained for the scanning pitch of 10 μm, while that for unfabricated surface was about 90 degrees.

Teflon inherently has the water repellent property, and this additional property given by the cotton-like micro structure has produced the superhydrohobic surface (contact angle >140degrees) on it.

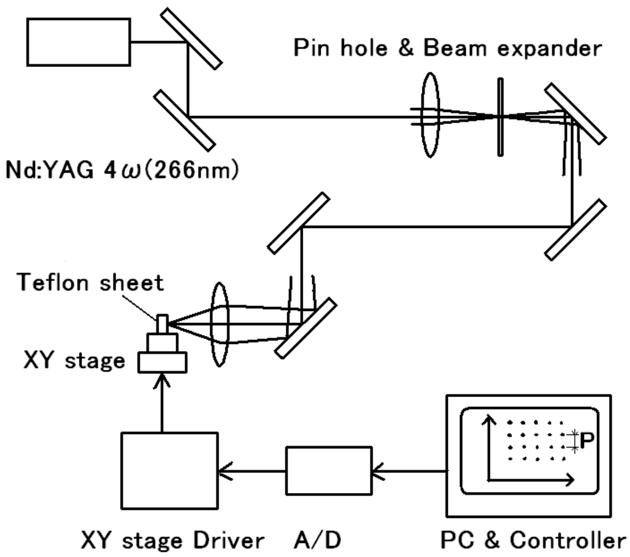

Fig 1 Experimental setup for generating a cotton-like surface on Teflon

The method described here is purely physical process, therefore the superhydrohobic surface obtained is considered to keep various valuable chemical characteristics of Teflon.

2. Experimental setup

The experimental setup is shown in Fig.1. The wavelength, pulse duration, focusing diameter and the energy of the laser were 266 nm, 10 ns, about 2 μm and about 0.1mJ, respectively. The beam quality of the laser was improved using a spatial filter (pin hole) and expanded to be about 10 mm in diameter. It was focused on the Teflon surface using a lens having a focusing length of 50 mm, and scanned two dimensionally using an automatic *x-y* micro stage with the scanning pitches of 10 μm～ 40 μm two dimensionally.

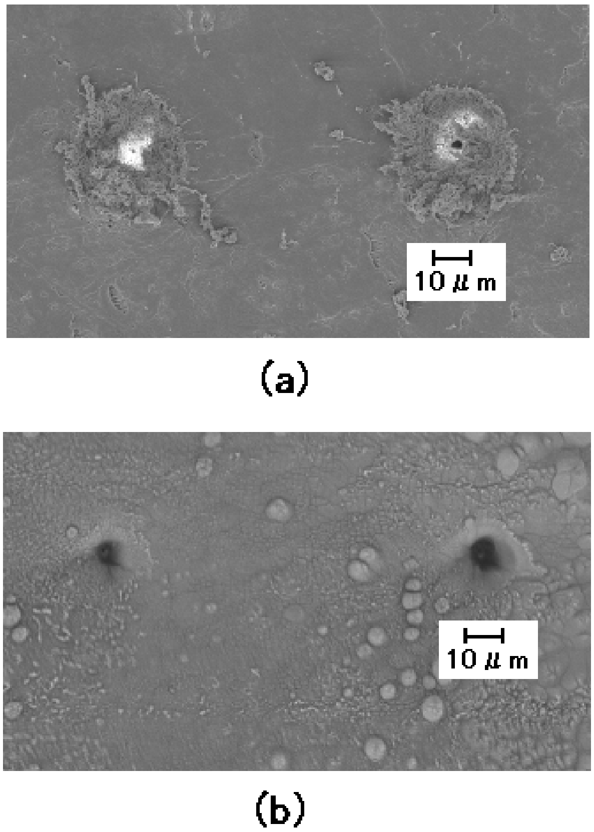

Fig.2 (a): Typical picture of the holes drilled on Teflon sheet by the focused laser beam and the debris surrounding them. (b) Typical SEM picture of the holes drilled on Polyimide sheet by the focused laser beam and the debris flying apart from the holes.

3. Experimental results

3.1 Fabrication of cotton-like microstructure

Fig.2 (a) shows the SEM (scanning electron microscope) picture of the holes drilled on the Teflon sheet by the focused laser beam and the debris surrounding them. That for Polyimide is shown in Fig. 2 (b) for comparison. In case of the former, the debris is fibrous (cotton-like) and does not fly apart from the hole, while the debris is dusty and flies apart from the hole in case of the latter.

When we used the fundamental wavelength of the Nd:YAG laser (1.06 μm), such type of fibrous debris was not observed, because the penetration depth of the laser beam for the wavelength of 1.06 μm is long due to the transparency of Teflon for this wavelength, and the specific absorbed laser energy into Teflon is not large enough to induce the thermal ablation. This type of ablation sometimes occurs, when the pulsed ultraviolet lasers are irradiated onto the polymers. Various works related to excimer laser ablation were reviewed by P. E. Dyer [12].

Fig.3 (a) shows the machined surface of the Teflon, where the holes are machined two dimensionally with scanning pitch of 15 μm. It can be easily seen that the surface is covered by fibrous debris and the morphology of the surface is drastically changed by the irradiation of the laser.

Fig. 3 (b) shows the magnified image of the corner of the machined surface. It can be seen that the fibrous debris

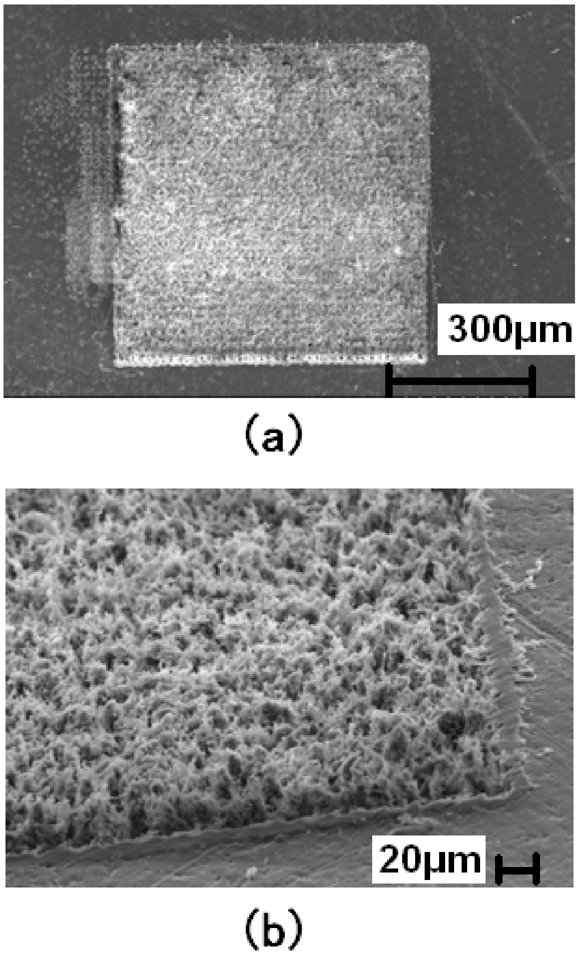

Fig.3. (a): Typical machined surface of the Teflon. The holes are machined two dimensionally with the pitch of 15 μm. (b): Magnified image of the corner of the machined surface.

does not fly apart from the machined area and the fibrous cotton-like surface was fabricated.

We think that chemical alterations, such as carbonization, did not occur on the Teflon surface by irradiating the laser beam judging from the fact that the color of this machined surface was not changed to be brown but to show stark white and Teflon has inherently strong chemical stability.

3.2 Estimation of hydrophobic characteristics

3.2.1 Contact angle of the water droplets

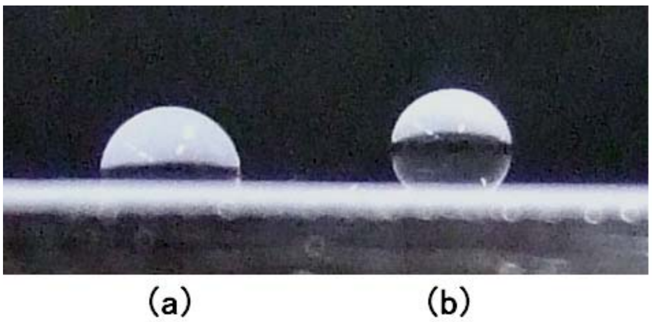

Fig. 4 Typical side view of the water droplets on the Teflon ((a): unmachined surface (contact angle is 90 deg.), (b):machined surface (Contact angle is 130 deg..))

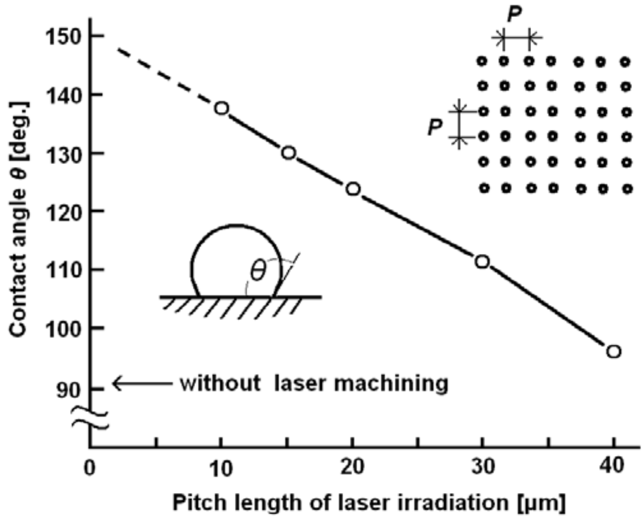

Fig. 5 Contact angles as a function of the pitch length of the laser irradiation.

Fig. 4 shows a typical side view of the water droplets on the surface of Teflon. (a) is a water droplet on the unmachined surface and (b) is the one on the machined surface. Teflon inherently has the water repellent property, therefore even the unmachined surface has relatively large contact angle of 100 -110 degrees [13]. In this experiment, it was measured to be about 90 degrees as shown in (a), which is slightly lower than the above value, probably due to the contamination on the surface.

It can be seen that the additional laser micro fabrication increases the contact angle up to 130 degrees as shown in (b).

Contact angles were introduced geometrically using the formula

$$\theta = 2 \cdot \tan^{-1}\left(\frac{h}{r}\right) \cdot \frac{180}{\pi} \qquad (1)$$

, where h is the height of the water droplet (the length between the top of the water droplet and the Teflon surface) and r is the radius of the contacting circular disk. The unit of the contact angle is given by degree. These values were measured observing the side view of the water droplets with the magnification mode of a commercial digital camera.

Fig. 5 shows the contact angles as a function of the pitch length of the laser irradiation. It can be seen that the contact angle increase as the pitch length decrease. The extrapolation of the pitch length to the shortest limit implies the potentiality to increase the contact angle as high as 150 degrees.

3.2.2 Superhydrophobic surface

Fig.6 shows a water droplet on the Teflon surface with cotton-like microstructure machined by the fourth harmonic of Nd:YAG laser (266nm). The scanning pitches of the laser irradiation were 10 μm, which was the shortest in this experiment. The contact angle was measured to be 140 degrees, which can be called “superhydrohobic” property. White part on the Teflon surface is the machined area.

Fig. 6 Water droplet on the superhydrohobic surface of Teflon. White part is the laser machined aria. (machined pitch:10 μm, contact angle:140 deg.)

4. Discussion

The reason why such type of the debris is generated is considered to be as follows. According to our preliminary experiment, the absorption length of Teflon was measured to be about 200 μm for the wavelength of 266 nm, while the most of the resins has the absorption length of a few μm or less for this wavelength. Due to the long absorption length of the laser beam, the absorption becomes not to be “surface absorption” type but becomes to be “bulk absorption” type. Therefore, the temperature of the irradiated parts does not increase high enough to fully dissociate the molecular structures of Teflon and finally ionize them.

If we assume the thermal process, the following phenomenon can be considered to occur. The temperature of the irradiated portion increases high enough to ionize or melt it partially, and the internal pressure generated by the increases in the temperature makes the melted parts expand apart from the hole as the debris.

On the other hand, if we assume the photochemical process, the following phenomenon can be considered to occur. The molecular binding of Teflon is partially separated by high photon energy of the ultraviolet laser to produce the fibrous structure. It is known that fibrous debris is generated, when KrF excimer laser (248nm) is irradiated on to the polymethyl, such as Polymethylmethacrylate, containing ultraviolet light absorber, such as Benzoin [1], [3], [6].

It is natural to think that the above mentioned phenomenon occur simultaneously, therefore the formation of the cotton-like structure described here can be considered to be induced by the complex process of thermal and photochemical.

The method described here is not a pure chemical process, but a physical process. Therefore, the chemical property of Teflon is expected to being kept and the water repellent surface obtained is considered to keep various important chemical characteristics of Teflon. This water repellant surface has the potentiality to be applied to various kinds of applications in the fields of micro liquid processing.

5. Conclusions

In conclusions, cotton like micro structure was selectively fabricated on the surface of Teflon by irradiating a focused fourth harmonic of Nd:YAG laser, which was found to have high water repellent property. The wavelength, pulse duration, focusing diameter and the energy were 266 nm, 10 ns, about 2 μm and about 0.1 mJ, respectively. The laser was irradiated with the pitches of 10 μm～ 40 μm. The maximum contact angle of about 140 degrees was obtained for the pitch of 10 μm, while that for unfabricated surface was about 90 degrees. This water repellant surface has the potentiality to be applied to various kinds of applications in the fields of micro liquid processing.

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(Received: March 20, 2010, Accepted: April 12, 2010)