PDMS surface modification using atmospheric pressure plasma

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We report an experimental study of the surface modification of polydimethylsiloxane (PDMS) by atmospheric pressure plasma (APP). The contact angle of a water droplet, scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR) were used to analyze the modified surface and the hydrophilic stability of PDMS samples, which were mixed with different ratios of base polymer and curing agent. The modified hydrophilic surface of PDMS lasted for 20 days, the duration of our experiment. In FTIR analysis, a broad peak at 3420 cm⁻¹ appeared after plasma treatment for 15 s, which corresponded to hydroxyl group formation on the PDMS surface during plasma treatment. Another new finding is that the magnitude of the peak for PDMS-05, which contained excess curing agent, was the smallest among the PDMS samples. Thus, the plasma treatment modifies the surface of the PDMS by adding hydroxyl groups and the resulting hydrophilic surface depends on the ratio of base polymer to curing agent. Moreover, SEM analysis showed that the bare PDMS-05 sample had a cracked surface, while the bare PDMS-20 was relatively smooth. This cracked or rough topology of the bare PDMS decreased with increased base polymer on reducing amount of curing agent. This improvement in the surface roughness of the plasma-treated samples may be caused by a shallow etching process that occurs during plasma treatment with oxygen gas. It constitutes an effective method for modifying the surface of PDMS without specific skills, expensive apparatus, or clean-room facilities.

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1. Introduction

Polydimethylsiloxane (PDMS) is used to fabricate microstructures using soft lithography because of its outstanding material properties. Oxygen plasma treatment to generate hydrophilic groups on the PDMS surface has been used to promote the structural bonding of PDMS to glass, silicon, and PDMS. However, the hydrophilic surfaces are unstable and quickly revert to their original hydrophobic states, because of the diffusion of low-molecular-weight (LMW) chains from the bulk PDMS to the oxidized surface [1]. Thus, the oxygen plasma method is rarely applicable to the precise alignment of thin PDMS film with a fine pattern or wafer-level alignment with a large area. Moreover, many of the process parameters require facilities that are too expensive for beginners in microfabrication.

Recently, there has been growing interest in the hydrophobic recovery of PDMS and development of long-term hydrophilic coating methods on PDMS substrates. Various methods to overcome the quick hydrophobic recovery have been studied, such as a method for eliminating LMW species [1], treatments with oxygen plasma [2], ultraviolet (UV)/ozone [3], UV-irradiation [4], and electrical discharge [5], the effects of the storage environment on hydrophobic recovery [6], and a multi-step modification method [7,8]. However, these techniques have various disadvantages, including time-consuming, complex processes, and the need for expensive facilities with vacuum apparatus and a DC power supply for high-voltage generation, safety problems, and well-trained technicians.

Another interesting modification method is radiofrequency (RF) plasma treatment at atmospheric pressure [9]. There are some advantages to atmospheric plasma processes, including that they are dry processes that do not produce chemical waste, there is highly efficient surface activation for various materials via the dual actions of radicals and charged particles, and they involve simple operations, consisting of pushing and pulling samples mounted on a moving stage for several seconds. Although atmospheric pressure plasma (APP) could be a very useful method for modifying PDMS surfaces, no quantitative study has yet been reported examining this. Thus, we investigated the influence of APP on the surface of PDMS for micro-electromechanical systems (MEMS) applications.

This paper presents the surface modification of PDMS by APP. The modified PDMS surfaces were analyzed using the contact angle of a water droplet, scanning electron microscopy (SEM), and Fourier-transform infrared spectroscopy (FTIR). For the quantitative study, PDMS samples with different mixing ratios of base polymer to curing agent were prepared and the results for bare and plasma-treated PDMS are compared and discussed.
2. Experimental

2.1. Sample preparation

Two types of PDMS (Sylgard 184, Dow Corning, Inc.) samples were prepared with different weight ratios of base polymer to curing agent (5:1 mixture of PDMS for PDMS-05, and 20:1 mixture of PDMS for PDMS-20). After mixing for 30 min, the liquid PDMS was poured into a Petri dish, degassed in a vacuum chamber, and cured at 75 °C for 4 h. The thickness of the PDMS samples was fixed at 1.47 mm in order to eliminate possible thickness effects on the PDMS surface modifications [6]. The PDMS plate was peeled off of the Petri dish and cut into the proper sizes to examine the contact angle of a water droplet and take SEM and FTIR measurements.

2.2. Plasma treatment

The contact angles of a water droplet on the surface of plasma-treated PDMS samples under various gas mixtures were measured to determine the effective gas mixture of argon and oxygen required to induce PDMS surface modifications. The prepared PDMS surface was modified using the scanning atmosphere RF plasma system (MyPL100, APP Co., Korea). In this system [10], argon and oxygen were used as a carrier and reactive gas, respectively. The effective plasma area was 0.9 cm wide and 10 cm long. The sliding speed and power were approximately 3 mm/s and 100 W, respectively. No thermal deformation of PDMS samples was observed after the argon/oxygen plasma treatment. Therefore, it was confirmed that the speed and power were appropriate for the surface treatment of PDMS samples without thermal deformation of the sample. The contact angles of the water droplet on the PDMS surface were measured using a contact angle analyzer (Phoenix 150, Surface Electro Optics, Korea) 2 h after plasma treatment. The volume of the droplet was 3 μL.

3. Results and discussion

3.1. Contact angle

Fig. 1 shows the measured contact angles of a water droplet on the surface of bare and plasma-treated PDMS under various flow rates of the oxygen gas in order to investigate its effect on the contact angle. A typical 10:1 mixture of PDMS samples was used. It was difficult to capture the images of the water droplet after the surface modification of PDMS using APP because the water droplet was almost completely spread out. In this paper, the contact angle was measured 2 h after the plasma treatment. The five measured values were averaged. The contact angle of the bare PDMS was 105.2°. The contact angles of the plasma-treated PDMS were much less than those of the bare PDMS. When the PDMS sample was treated using argon/oxygen plasma with the gas mixture of argon to oxygen at a ratio of 5000:25, the contact angle and the standard deviation were smallest compared with other cases. However, considering the standard deviation of the measured data, the effect of the flow rate of the oxygen gas in argon/oxygen plasma on the contact angle was very minor in our experiment. Thus, in this work, it was concluded that a 5000:25 ratio of the gas mixture of argon to oxygen was preferable for the surface modification of PDMS samples.

This hydrophilic property of PDMS is highly correlated with the change of its surface composition after the plasma treatment. After plasma treatment, the intensity of the carbon peak decreases significantly while oxygen peak increases [9]. Compared with previous work [2], the measured contact angle of the water droplet on the surface of PDMS samples modified with ICP RIE and PECVD was close to our results in Fig. 1. However, unlike in our case, the measurement of the contact angles was performed within the first minute after the plasma treatment because of the rapid recovery of the hydrophobic property of PDMS.

3.2. Hydrophobic recovery

Fig. 2 shows the measured contact angles of a water droplet on the surface of bare and plasma-treated PDMS. One-week-old PDMS samples were exposed to APP, and the contact angle was measured. The plasma treatment process was the same as that described in Fig. 1. The five measured contact angles were averaged. As shown in Fig. 2a, the contact angle of the bare PDMS-05 was 107.8°, while the contact angle of PDMS-20 was 99.2°. The contact angle gradually increased as the increment of the curing agents changed. This change was caused by excess silicon hydride groups and one vinyl group on the PDMS surface; the amounts depend on the mixing ratio of the base polymer and the curing agent [11]. For the plasma-treated PDMS shown in

![Fig. 1. Contact angles of a water droplet on the surface of bare and plasma-treated PDMS under various flow rates of oxygen gas. (a) Bare PDMS and (b-d) plasma-treated PDMS.](image)
Fig. 2b and c, the contact angle dramatically decreased because the surface of PDMS samples was strongly affected by the plasma and modified by the strong hydrophilic surface. The contact angles of all samples slowly increased with time. Another interesting observation is that the measured contact angles of the plasma-treated samples showed trends similar to those of the bare PDMS: all samples depended on the PDMS mixing ratio.

Fig. 3 shows the summarized contact angle results for a water droplet on the surface of plasma-treated PDMS samples with different mixing ratios as a function of time. As previously discussed, the measured contact angles of PDMS-05 were larger than those of PDMS-20. Following plasma treatment, all samples showed strong hydrophilic properties, and the modified surfaces lasted for the duration of our measurement time.

3.3. FTIR spectra

Fig. 4 shows the FTIR (Spectrum GX system, Perkin Elmer, USA) spectra of the surface of plasma-treated PDMS samples. The surfaces of the PDMS samples were immediately examined within Fig. 4. FTIR spectra of bare and plasma-treated PDMS-05 and PDMS-20 samples. (a) FTIR spectra in the full measurement range; (b) FTIR spectra from 3900 to 2700 cm⁻¹.
30 min of plasma treatment. Compared with the FTIR of the bare PDMS, a broad peak at 3420 cm\(^{-1}\) appeared after plasma treatment, while the peaks at 2963 and 2905 cm\(^{-1}\) observed for the bare PDMS did not change. The new peak corresponded to hydroxyl groups that formed on the PDMS surface during plasma treatment. This result was similar to that of the attenuated total reflectance (ATR)–FTIR spectra of PDMS samples treated using microwave plasma for 4 min\(^{[12]}\). Another new finding is that the magnitude of the peak for PDMS-20 was larger than that for PDMS-05. Therefore, the plasma treatment can modify the PDMS surface by adding hydroxyl groups, and the resulting hydrophilic surface depends on the mixing ratio of the base polymer to curing agent. Thus, as shown in Fig. 2, the contact angle of a water droplet on the modified surface of various PDMS samples depends on its mixing ratio.

### 3.4. SEM observations

Fig. 5 shows SEM (Hitachi S-4700, Hitachi, Japan) images of the bare and plasma-treated PDMS samples. The bare PDMS-05 sample (a-1) had a cracked surface, and the bare PDMS-20 (b-1) was relatively smooth. This cracked or rough topology of the PDMS decreased with the increments of base polymer by reducing the curing agent. Based on our experience, excessive curing agent results in low viscosity in the liquid PDMS and high rigidity in the cured silicon-hybrid PDMS. The base polymer and curing agent are mixed thoroughly, and the polymerization of liquid PDMS proceeds excessively during the curing process, which is a direct heating method performed on a hotplate. Thus, the surface of PDMS-05 appeared to contract during the curing process of liquid PDMS when excessive curing agent was present. Other PDMS samples also contracted or showed a cracked surface; however, the relative roughness of these samples was less than that of PDMS-05. Although not shown here, the surface topology and the contact angle were also dependent on the curing time and temperature. Compared with the surface profile of PDMS samples cured at room temperature, the surface roughness of both PDMS-50 and PDMS-20 samples cured at 120 °C for 180 min increased with the increments of the curing temperature and time. This phenomenon results in the increment of the contact angle and the decrement of
the wettability of hydrophobic PDMS. Unlike the bare PDMS, none of the surfaces of the plasma-treated PDMS samples were cracked.

Fig. 6 shows the surface profiles of bare and plasma-treated PDMS samples obtained from the SEM images in Fig. 5 using ImageJ software. PDMS-20 had a smoother surface than PDMS-05. More interesting was that the surfaces of both plasma-treated PDMS samples were very rough compared to the bare ones. This improvement in the surface profile may have been caused by a shallow etch process during plasma treatment with oxygen gas.

4. Conclusions

In this paper, the surface of PDMS was modified using atmospheric pressure plasma, and the modified surfaces of PDMS films were analyzed using the contact angle, SEM, and FTIR. Contact angle measurements showed long-term hydrophilic stability of the product for up to 20 days, with a contact angle of approximately 75° for the plasma-treated PDMS-20 samples, while the contact angle without plasma treatment was 99.2°. FTIR showed a broad peak at 3420 cm⁻¹, corresponding to hydroxyl groups that appeared after plasma treatment for 15 s. Using SEM, the surface roughness of the plasma-treated PDMS samples was improved, compared with the bare PDMS, because of the shallow etching process that occurs during plasma treatment with oxygen gas.

In short, the hydrophilic nature of the PDMS surface can be modified quickly using plasma treatment at atmospheric pressure. The hydrophilic surface depends on the mixing ratio of base polymer to curing agent. A PDMS sample with excess base polymer shows long-term hydrophilic stability with a low contact angle and a relatively smooth surface roughness with a small standard deviation.

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References