Ultrahydrophobic Surface Formation on Materials by Plasma Improvement

Masaaki Katoh, Norihisa Kanoh, Akira Kojima and Takeo Ohte

Gunma National College of Technology, 580 Toriba-cho, Maebashi-shi, Gunma 371, Japan

Ultrahydrophobic surface formation on materials without changes with the passage of time by plasma improvement has been successfully achieved. The contact angle with water became approximately 160°. It is very important and useful to form the ultrahydrophobic surface such as the lotus surface because it is used in various fields. We used polytetrafluoroethylene (PTFE), polymonochlorotrifluoroethylene (PCTFE), and perfluoroalkoxy (PFA) as materials and treated them by CF4 plasma or CHF3 plasma. In order to investigate the effects of the ions and the radicals in the plasma, the treatment apparatuses of two types were used. One (apparatus I) was the type of parallel plate electrodes and the other (apparatus II) was the induction type. The estimation of material surface characteristics was carried out by measurements of the contact angle of the material surface with water, the weight of the materials and SEM observation. In case the materials were placed on the power electrode in the apparatus I and the input power for the improvement was large, ultrahydrophobic surfaces without change with time were produced. In case of PFA, such surfaces were formed even if it was put on the earth electrode. Such surfaces were not made by using the apparatus II. It was found that the formation of ultrahydrophobic surfaces without change with time could be attained by the following methods. (1) Plasma that has fluoric ions and fluoric radicals as its composition elements should be used. (2) Sheath voltage between the plasma and the material should be large (high). The roughness on the surface and the stable bond between fluoric atoms and atoms of the material on the surface should be formed. (3) Material whose structure is suitable for becoming ultrahydrophobic should be used.

Keywords: ultrahydrophobic surface, change with time, fluoric plasma, fluoric polymers, surface roughness, stable F atoms

1. Introduction

Surface improvement of materials by cold plasma has widely been used in various fields [1][2]. It can give useful characteristics to material surfaces. Ultrahydrophobicity is a typical characteristic. Ultrahydrophobic [3][4] surface is defined as one whose contact angle with water on the surface exceeds 150°. The ultrahydrophobic technology broadly attracts attention, and it is studied in fields such as hydrophobic materials, cars and medical care machinery [5]. The chemical absorption [3] and dispersion plating [6] were used as techniques for making the ultrahydrophobic surface on various materials in many fields.

The cold plasma (low-temperature plasma) has reactive composition elements and can make various effects on material surfaces. The surface improvement by cold plasma has the following merits. The treatment time is short. This is a dry process. There is no generation of heat by the improvement. The damage by treatment is small. However, this improvement has some problems. The control of material surface characteristics is difficult, and the surface characteristics after modification change with the passage of time [7].

In this study, we controlled wettability of material surfaces on fluoric polymers and tried to form the ultrahydrophobic surfaces on the polymers without the change with time after the plasma treatment (no elapsed change; there is no change even if time passes) by using cold plasma. In order to attain this aim of study, the requirements (methods) for producing the
ultrahydrophobic surface have been investigated from the standing points about both the plasma and the material.

2. Method
2.1 Materials
We used fluoric polymers (PTFE, PCTFE, PFA). Each material was washed with alcohol and water, and then dried before it was used.

2.2 Plasma improvement
Cold plasma treatment was carried out by R.F. glow discharge plasmas. As shown in Fig.1, the plasma apparatus I with parallel plate electrodes (Nichiden Anelva, the modified version of PIA-200) was used for treatment. This plasma apparatus has a power electrode (4 in Fig.1; stainless steel $\phi$ 95 mm), and an earth

Fig. 1 Plasma apparatus I for treatment.
(This is the type which has the parallel plate electrodes.)

<table>
<thead>
<tr>
<th>Table 1 Treatment conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
</tr>
<tr>
<td>Frequency</td>
</tr>
<tr>
<td>Power</td>
</tr>
<tr>
<td>Gas</td>
</tr>
<tr>
<td>Gas flow rate</td>
</tr>
<tr>
<td>Power electrode diameter</td>
</tr>
<tr>
<td>Earth electrode diameter</td>
</tr>
<tr>
<td>Electrode spacing</td>
</tr>
<tr>
<td>Plasma treatment time</td>
</tr>
<tr>
<td>Sample</td>
</tr>
</tbody>
</table>
electrode (6; stainless steel φ 92 mm) in a stainless steel discharge vessel (3; inside diameter 150 mm). R.F. power from a R.F. electric power source is supplied to the power electrode through a matching box with a blocking condenser (2). Samples were put on the earth electrode or attached to the power electrode. The discharge (treatment) chamber was evacuated to a high vacuum in advance. The plasma gases used for this improvement were CF₄ and CHF₃. The mass flow of gas was controlled in 50 sccm. Then, a designated power (13.56 MHz) was supplied to the electrodes. R.F. discharge plasma was generated. Treatment conditions for this improvement were shown in Table 1. Another apparatus which we were named plasma apparatus II (Samco, Model: BP-1) was also used for plasma treatment. This one was an induction type.

2.3 Measurement of surface characteristics
2.3.1 Contact angle on the surface
The contact angle with water at room temperature on each plate surface before and after the plasma treatment was measured by a goniometer-type contact angle meter (Erma, G-I) in order to estimate plasma-treatment effects (the condition of ultrahydrophobicity).

2.3.2 Measurement of the weight
We measured the weight of the each material by using an electronic balance (Shimazu DIRECT READING BALANCE NL-DTP).

2.3.3 SEM observation
The morphology of the each material was observed by a scanning electron microscopy (SEM, Hitachi, S-2050) before and after plasma treatment.

3. Results
3.1 Treatment by plasma apparatus I
The contact angle of PTFE plate before plasma treatment was about 105°, that of PCTFE plate was about 95° and that of PFA plate was about 100°. These plates were treated by CF₄ plasma for the first time. Fig.2 shows the contact angles after the treatment. The contact angle 150° is shown on the dotted line. With 100 W, The contact angles of all materials increased to about 160° when they were placed on the power electrode, and ultrahydrophobic surfaces were formed. After the treatment, the contact angle of the material surfaces that was placed on the power electrode was larger than that of the materials placed on the earth electrode. In case it was put on the earth electrode, ultrahydrophobic surface was formed only for PFA. The treatment effect might be different with every material.

Fig.3 shows the changes of PTFE plate surfaces at room temperature with the passage of time after the plasma treatment in case the material was placed on the power electrode. When the treatment power was small the change with time occurred and the contact angle difference between the value ten minutes
Fig. 3 Changes of contact angles at room temperature with the passage of time after the plasma treatment. (PTFE, Plasma apparatus I for treatment, power side, CF₄ plasma, 13.3 Pa, 50 sccm, treatment time 10 min., □: 10 min. later, ○: 1 week later)

Fig. 4 Decreases of the weight after the plasma treatment. (PTFE, Plasma apparatus I for treatment, CF₄ plasma, 13.3 Pa, 50 sccm, 10 min., □: power side, ○: earth side)

Fig. 5 SEM photographs of the PTFE surfaces treated by CF₄ plasma. (apparatus I for treatment, input power: 50 W (small), 100 W (large), pressure: 13.3 Pa, gas flow rate: 50 sccm, gap: 5 cm, treatment time: 10 min.)
A: Untreated material, B: material on the earth electrode, C: material on the power electrode.
after the treatment and that one week after the treatment was about 15° at room temperature with the input power of 20 W. However, this change did not occur if the treatment power was large (100 W).

Fig. 4 shows the decreases of the weight of the material after the plasma treatment. After the plasma improvement, the weights decreased in both electrode sides. When the treatment power was increased, the decrease of the material weight increased rapidly in the material placed on the power electrode, but it did not change very much in case the material was put on the earth electrode side. The inclinations of the differences of the treatment effects with kinds of the materials were hardly found (existed).

Fig. 5 shows the results of observation of PTFE surfaces using SEM. Roughness was formed on the surfaces after the plasma improvement. The etching by CF4 plasma more advanced on material placed on the power electrode than that on the earth electrode. The inclinations of the differences of the treatment effects with kinds of the materials were hardly found (existed).

Table 2 Contact angles of PTFE after the plasma improvement. (PTFE, apparatus I, CHF3 plasma, 13.3 Pa, 50 sccm)

<table>
<thead>
<tr>
<th>Power</th>
<th>50 W, 10 min.</th>
<th>100 W, 10 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min. later</td>
<td>143.5°</td>
<td>153°</td>
</tr>
<tr>
<td>1 week later</td>
<td>137°</td>
<td>155°</td>
</tr>
</tbody>
</table>

Table 3 Contact angles of PTFE after the plasma improvement. (PTFE, apparatus II, CF4 plasma, 13.3 Pa, 50 sccm)

<table>
<thead>
<tr>
<th>Power</th>
<th>20 W, 10 min.</th>
<th>50 W, 10 min.</th>
<th>100 W, 1 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min. later</td>
<td>105.5°</td>
<td>111°</td>
<td>133°</td>
</tr>
<tr>
<td>1 week later</td>
<td>95°</td>
<td>107°</td>
<td>128°</td>
</tr>
</tbody>
</table>

decreased one week later, and the change with time occurred. But if the treatment power became large, the change with the passage of time did not occur.

3.2 Treatment by plasma apparatus II

Table 3 shows the value of the contact angles with CF4 plasma treatment by using the plasma apparatus II. When materials were treated with the plasma apparatus II, the contact angle did not rise very much. We treated PTFE with 100 W for 1 hour, but the contact angle rose only to 133°. Ultrahydrophobic surfaces were not formed. In addition, the change with time has occurred even if the treatment power was large.

4. Discussion

Ultrahydrophobic surfaces were formed in case the materials were placed on the power electrode in the apparatus I (the type of parallel electrodes) by more than 50 W of the input power. The change of the contact angle of the ultrahydrophobic surfaces with the passage of time after the plasma improvement was very small by modifying it with large power (100 W). However, this change existed in small power treatment. Ultrahydrophobic surfaces were not formed in case the materials were put on the earth electrode in the apparatus I except that the PFA was treated by the large power. When the materials were improved by
using the apparatus II (the type of induction, 100 W), its surface did not become ultrahydrophobic. In the apparatus I, the sheath voltage between the plasma and the material on the power electrode side is larger than that between the plasma and the material on the earth electrode side, and is larger than that in case of the apparatus II. In case the sheath voltage is large, the ions in the plasma are accelerated by this voltage and collide with the material with high energy. It may be considered that the roughness of the material surface increases by the reaction (etching) with this bombardment of the high energy ions, and that the stable fluoric atoms, which do not secede from the material surface even if time passes, also increase by this effect. When the bombardment energy of the ion is small, the unstable fluoric atoms are introduced to the material surface. Because these unstable atoms secede from the surface with the passage of time, the elapsed change occurs. Therefore, in producing the ultrahydrophobic surface the effect of ions is larger than that of radicals.

However, in case the material was PFA, its surface became ultrahydrophobic (100 W) although it was placed on the earth electrode. This means that there is the surface (material), whose structure is suitable for becoming ultrahydrophobic.

The difference (comparison) of the effect between CF\textsubscript{4} plasma and CHF\textsubscript{3} plasma was as follows. CF\textsubscript{4} is a gas that has the etching effect and CHF\textsubscript{3} is a gas that has the deposition effect. In case of using CF\textsubscript{4} plasma, the material surface was etched and the roughness was formed in the inner part of the material. Though the surface became ultrahydrophobic, the strength of the material might decrease a little. Therefore, the optimum condition may exist for CF\textsubscript{4} plasma treatment. When CHF\textsubscript{3} plasma was used, the deposited film, which had much roughness, was produced on material surface.

It was found that the formation of the ultrahydrophobic surface without the change with the passage of time could be attained by the following methods (conditions).

(1) Plasma that has fluoric ions and fluoric radicals as its composition elements should be used.

(2) Sheath voltage between the plasma and the material should be large (high). The roughness on the surface and the stable bond between fluoric atoms and atoms of the material on the surface should be formed.

(3) Material whose structure is suitable for becoming ultrahydrophobic should be used.

5. Conclusion

We could find the method to form the ultrahydrophobic surface without the elapsed change. This was way how the material whose structure was suitable for becoming ultrahydrophobic was used and the ions which had fluorine atoms collided with the material surface with the large energy. The roughness was formed in the inner part of the material by CF\textsubscript{4} plasma treatment. In case of CHF\textsubscript{3} plasma improvement the roughness of surface film was produced on the material surface. In this study, its mechanism could also be made clear.

References