Dynamic Plasma CVD and Preparation of Functional Organic Thin Films

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This paper describes the chemical and morphological properties of super water-repellent surface of solid materials prepared by a 13.56 MHz inductively coupled plasma using fluorohydrocarbons such as vinylidene fluoride and 1,1,1,2-tetrafluoroethane. Through the reaction initiated by the electron impact into fluorohydrocarbon molecules, fluorine-containing and hydrophobic polymers grew in the gas phase to deposit on substrates. The morphology of deposits seems to depend on hydrophilicity or hydrophobicity of substrates. The more hydrophilic substrate may maintain the smaller granular structure than ca. 100-nm diam. However, polymer granules may be expanded radially by surface tension and get into flat on hydrophobic substrates. Dynamic plasma CVD we proposed enabled us to control the size of deposited granules on the surface to be smaller and improve the fluorine content to be richer. Thus, we could easily obtain super water-repellent thin film with gradation in granular size and chemical compositions.

Keywords: super water repellency, thin film, fluorohydrocarbons, plasma polymerization

1. Introduction

It is useful to provide a specific chemical function to materials surface. For instance, water repellency has been required in various fields, and so extensive studies concerning the preparation of water-repellent surface have been carried out to date. Takai et al. and Hozumi et al. reported a series of studies on transparent and water-repellent organic thin films derived from fluoroalkylmethoxysilanes by using plasma-enhanced chemical vapor deposition (PECVD) technique.[1-3] Petasch et al. vented water repellency in polyester yarn by hexamethyldisiloxane and tetramethylsilane plasma polymerization [4], and Iriyama et al. prepared water-repellent nylon fabrics by fluorocarbon plasma.[5] Recently, super water repellent surface whose contact angle against water drop exceeds 150 degrees has become major interest in particular. From that point of view, we have reported the preparation of super water-repellent non-woven fabrics by radio-frequency (RF) plasma involving electrons and photons using fluorohydrocarbons (FHC).[6]

In this paper, we propose a unique method to prepare an organic thin film displaying super water repellency especially at the outermost surface of the film. The method involves a dynamic plasma polymerization and deposition in a final finishing process, which is executed, for example, by letting FHC vapor pressure increase rapidly until plasma disappears. We call such a preparation method the dynamic plasma CVD because a plasma parameter dynamically changes in a process. The dependence of the super water repellency on the chemical and morphological properties of the dynamic plasma CVD films were examined by the X-ray
photoelectron spectroscopy (XPS) and the scanning electron microscope (SEM).

2. Method
2.1. Apparatus and samples

The plasma apparatus used was consisted of a 13.56-MHz RF generator, an RF power meter, a tuner, a copper coil tubing, and a 4.5-cm outer diam. and 50-cm length Pyrex reactor tube equipped with vacuum gauges, gas pressure control valves, and mass flow controllers via taper joints. Square quartz glasses (10-mm side length and 1-mm thickness) and rayon and polyester nonwoven fabrics (10-mm side length) were used as solid substrate samples. They were placed at three positions in the reactor tube, i.e. 5-cm upstream from the end of the copper coil tubing, at the center of the copper coil tubing and 5-cm downstream from the end of the copper coil tubing. The reactor tube was evacuated below 0.1 Pa and then gaseous FHC such as vinylidene fluoride (VDF) and 1,1,2-tetrafluoroethane (TFE) was introduced into the reactor tube through a gas inlet in upstream from the coil. An inductively-coupled plasma was generated on 1-100 Pa FHC vapor.

\[
\begin{align*}
\text{H} & \quad \text{C=CF} \quad \text{F} \\
\text{H} & \quad \text{F} \quad \text{H} \quad \text{C} \quad \text{C} \quad \text{F} \\
\text{VDF} & \quad \text{TFE}
\end{align*}
\]

2.2. Conventional and dynamic plasma CVDs

Conventional plasma CVD was carried out under a constant FHC gas flow and pressure. On the other hand, dynamic plasma CVD was performed under increasing gas flow and pressure in the final stage of CVD treatment until plasma emission disappeared as shown in Fig. 1, which illustrates VDF pressure change during a dynamic plasma CVD, that is, VDF gas pressure began to increase at the time point (a) and plasma emission disappeared at (b) reaching 185 Pa after the treatment started with RF plasma generated under the following conditions: \( P \), 40 W; \( r_{\text{TFE}} \), 20 cm\(^3\)min\(^{-1}\); and \( P_{\text{VDF}} \), 130 Pa, the gas pressure was measured with a Piranay vacuum gauge.

Typical parameters in dynamic plasma CVD were RF power \( (P) \), FHC flow rate \( (r_{\text{FHC}}) \), gas pressure \( (p) \), conventional plasma treatment time \( (t_c) \), and dynamic plasma treatment time \( (t_d) \) during which plasma emission could be still observed after FHC gas pressure began to increase.

![Fig. 1. VDF gas pressure change in dynamic plasma CVD.](image)

Substrates were kept at room temperature during CVD treatments.

2.3. Surface analysis

Water repellency was estimated by measuring the contact angle against a 1.6-mm diam. water drop with a contact angelometer (Kyowa Kaimenkagaku Co. Ltd., type FACE CA-D). Morphological observation was performed by a field emission scanning electron microscope (JEOL Co. Ltd., FE SEM, type JSM-6330F) and the qualitative and quantitative surface chemical properties concerning to existing elements and chemical bonds were obtained by the X-ray photoelectron spectroscopy (Phi Co. Ltd., ESCA, type Quantum 2000).

3. Results and Discussion

3.1. Difference between conventional and dynamic plasma CVD in preparing super water-repellent thin films

Typical results were shown in Table 1. The contact angle of a water drop against untreated quartz glass was ca. 13°. This result is consistent with the generally accepted idea that the surface of quartz is hydrophilic owing to hydroxyl groups. Rayon, which is regenerated cellulose, is hydrophilic itself. Untreated rayon nonwoven fabrics easily absorbed water drops and gave the zero-degree contact angle of water drops. On the other hand, polyester that has the ester bonding in the chemical structure is less hydrophilic, so the nonwoven fabrics gave a large contact angle. The value reached 141° in our experiment, which
Table 1. Contact angle and morphological characteristics of thin films prepared by HFC plasma CVD

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\theta_1^{a}$</th>
<th>Gas$^c$</th>
<th>Plasma$^d$</th>
<th>$t_{Pl}^{e}$</th>
<th>$t_{Pl}^{f}$</th>
<th>Contact angle$^f$</th>
<th>$d^{h}$/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\theta_1$</td>
<td>$\theta_2$</td>
<td>$\theta_3$</td>
<td>2</td>
</tr>
<tr>
<td>Quartz</td>
<td>13$^b$</td>
<td>VDF</td>
<td>Conventional</td>
<td>10</td>
<td>0</td>
<td>90$^o$</td>
<td>165$^o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VDF</td>
<td>Dynamic</td>
<td>1</td>
<td>42</td>
<td>89$^o$</td>
<td>165$^o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TFE</td>
<td>Conventional</td>
<td>10</td>
<td>0</td>
<td>0$^b$</td>
<td>99$^o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TFE</td>
<td>Dynamic</td>
<td>1</td>
<td>30</td>
<td>91$^o$</td>
<td>93$^o$</td>
</tr>
<tr>
<td>Rayon</td>
<td>0$^b$</td>
<td>VDF</td>
<td>Dynamic</td>
<td>1</td>
<td>35</td>
<td>-</td>
<td>139$^o$</td>
</tr>
<tr>
<td>Polyester</td>
<td>141$^{b}$</td>
<td>VDF</td>
<td>Dynamic</td>
<td>1</td>
<td>35</td>
<td>-</td>
<td>147$^b$</td>
</tr>
</tbody>
</table>

$^a$Contact angle of untreated substrate. $^b$Water drop was absorbed. $^c$FHC gas: VDF, 20 cm$^3$/min$^1$SATP, TFE, 30 cm$^3$/min$^1$SATP.
$^d$13.56 MHz, 40W. $^e$Symbols $t_1$ and $t_2$ represent conventional plasma treatment time and dynamic plasma treatment time, respectively.
$^f$Contact angle measured at 5-cm upstream from the coil ($d_1$), the center of the coil ($d_2$), and 5-cm downstream from the coil ($d_3$).
$^g$Contact angle larger than 165°, the measurement limit of our system. $^h$Diameter of granular structure grown at the center (2) and 5-cm downstream from the coil (3), estimated from SEM images.

indicates that the fabrics is a high water-repellent material itself. Dynamic plasma CVD treatments using VDF or TFE generally gave an increase in the contact angle of water drops against those materials. The CVD treatment seems remarkably effective especially on hydrophilic surface of materials, but little effect on hydrophobic surface of materials. The extent of increase in contact angle depended on the kind of FHC gas used, the treatment method whether conventional or dynamic plasma CVD, and the position in the reactor tube. In the Table 1, >165° represents the super water-repellent surface getting the larger contact angle than 165° by the CVD treatment. The value of 165° was the upper-side limit of our contact angle measurement system. Such a super water-repellent thin film was reproducibly formed in downstream from the copper coil tubing.

3.2. Effect of reactivity of organic monomers

When using TFE monomer, the region forming super water-repellent thin film shifted more downstream than in the case using VDF. The shift may be attributed to the difference of the chemical reactivity between TFE and VDF molecules, that is, the polymerization rate of TFE consisting of only single bonds may be so slower than VDF possessing a double bond. The detailed study on the reaction mechanism is vigorously in

![SEM images](image1.png)

**Fig. 2.** SEM images ($\times$ 50,000) of granular-structured thin films formed by VDF conventional plasma CVD (a) and dynamic plasma CVD (b) on quartz substrate: RF power $P$, 40 W, VDF flow rate $r_{VDF}$, 20 cm$^3$/min$^1$SATP.
3.3. Comparison with SEM images

The dynamic plasma CVD seems more effective than a conventional method to originate super water-repellent function on any materials. The tendency can be explained by SEM observations. See Fig.2, which reveals that granular structures formed by dynamic plasma CVD was minuter than those grown in conventional plasma CVD.

3.4. XPS analysis and evaluation

Yellowish polymers deposited on substrates set upstream from the copper coil tubing during both conventional and dynamic plasma CVD treatments. Contact angle measurements with water drops showed these polymers were carbonaceous as presenting ca. 90° contact angle or sometimes extremely hydrophilic because of 0° contact angle.

XPS spectra shown in Fig. 3 clearly indicate that polymer deposited at the upstream position 1 contained relatively larger amount of oxygen than polymers deposited at any other positions in the reactor. Especially note that super water-repellent polymer deposited at the downstream position 3 contained very few oxygen atoms.

These results indicate that defluorination, carbonization, and oxidation reactions simultaneously proceeded with polymerization because of small amount of air leaking into the reactor tube through upstream joint connectors to make deposition of carbonaceous, oxygen-containing, yellowish and sometimes extremely hydrophilic polymers on substrates.

Fig. 4 shows the XPS depth profile of super water-repellent polymer film prepared by VDF dynamic plasma CVD on a quartz substrate set at the position 2. It reveals that the chemical composition is gradating toward the depth. The fluorine concentration exponentially increases toward the surface and reaches maximum at the surface. Such gradation in the fluorine composition may make an important role to form the minute granular structure containing rich fluorine atoms at the surface to make it super water-repellent.

4. Conclusion

The formation mechanism of super water-repellent thin film can be illustrated as Fig. 5 on the basis of above discussions.

The reaction may be initiated by the electron impact into FHC molecules [6]. Then, hydrophobic fluorine-containing polymers grow in the gas phase to be deposited on substrates. The morphology of
deposits seems to depend on hydrophilicity or hydrophobicity of substrates. The more hydrophilic substrate may maintain the smaller granular structure than ca. 100-nm diam. However, polymer granules may be expanded radially by surface tension and get into flat on hydrophobic substrates.

Conclusively, dynamic plasma CVD enabled us to control the size of deposited granules on the surface to be smaller and improve the fluorine content to be richer. Thus, we could easily obtain super water-repellent thin film with gradation in granular size and chemical compositions.

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