Improvement of Adhesive Strength of Polytetrafluoroethylene by Defluorination Treatment with Combination of Atmospheric Pressure Glow Plasma Treatment and Chemical Transport Method

Masuhiro Kogoma, Kazuo Takahashi and Kunihiro Tanaka

Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo, Japan
tanaka@mls.sophia.ac.jp

Polytetrafluoroethylene (PTFE) sheet surface was treated by the diborane/H₂/He plasma for the deflurination to improve the adhesive strength. Diboran was generated by the H₂/He plasma treatment of a boron plate and was transported to the plasma zone for PTFE sheet treatment. And then, the defluorination plasma treatment with this diborane/H₂/He mixture gas performed PTFE sheet. Fluorine atom content of treated PTFE surface was decreased to about twentieth of that of untreated PTFE. The adhesive strength between treated PTFE and epoxy glue became stronger enough for practical use.

Keywords: polytetrafluoroethylene, surface treatment, defluorination, atmospheric pressure glow plasma, chemical transport method

1. Introduction
Fluorinated polymers such as polytetrafluoroethylene (PTFE) have many unique characteristics: for example, high chemical resistance, high dielectric constant, high heat resistance and low coefficient of friction. Thus, they have been used as typical inert materials for many situations, such as packaging materials. They have a big problem, however, the difficulty of the paint and adhesion. Some agents that contain metallic sodium are often used for surface treatment of these polymers to improve the paint and adhesion. However, this treatment needs a large amount of cleaning water and the disposal of much waste fluid. Moreover, their surfaces become blackish through the wet treatment. So a new dry process instead of the wet treatments has been desired.

The glow plasma, which is the most typical low temperature and weakly ionized plasma, can be used for this treatment as a dry method since it has a spatially uniform plasma region and higher densities of active species than those of silent or corona discharges. The atmospheric pressure glow (APG) plasma technique can generate a spatially uniform plasma even at atmospheric pressure if only one uses a high frequency generator of more than 1 kHz, electrodes whose surfaces are covered with dielectric plates and a sample gas diluted with a large amount of helium gas [1-3].

In our previous studies, the APG plasma treatment was found to be able to improve the adhesion strength between some kinds of fluorinated polymer films and epoxy glue [4-7]. Generally, the low surface energies of the fluorinated polymers lead to the low adhesive strength between such polymers and glue, and the fluorine atoms on the fluorinated polymer surface lead to the low surface energy of the polymers [8]. We considered that the fluorine atoms generated through the dissociation of C-F bonds by the plasma needed to be changed into a gaseous compound by reacting with some reactants, and that the gaseous compound had to be removed from the polymer surface as fully as possible.
Boron trifluoride ($\text{BF}_3$) is one of the gaseous fluorine compounds at room temperature and the bond enthalpy of fluorine with boron ($757 \text{ kJ mol}^{-1}$) is bigger than that of fluorine with hydrogen or carbon ($570$ or $552 \text{ kJ mol}^{-1}$) [9]. Thus, in previous study, the $\text{H}_2/\text{He}$ plasma treatment with diborane, which was generated by the $\text{H}_2/\text{He}$ plasma treatment of boron plate (chemical transport method), was used for the defluorination of PTFE and the fluorine atoms were removed from PTFE surface almost completely [7].

In this study, we tried to examine the effect of the defluorination treatment for the improvement of the adhesiveness of PTFE.

2. Experimental

Fig. 1 shows the discharge apparatus which had two discharge areas. The discharge areas were bounded for quartz glass plates, and so $\text{H}_2/\text{He}$ mixture gas flowed in one direction. The upstream and downstream discharge areas were used for diborane generation and PTFE surface treatment, respectively. The boron plate (thickness, about $0.1 \text{ mm}$) was prepared by solidification of boron powder ($0.3 \text{ g}$) with inorganic adhesive ($0.3 \text{ g}$, Aron Aloha Inc., Aron Ceramic D). PTFE sheet, whose sizes were $20 \text{ mm} \times 20 \text{ mm} \times 0.2 \text{ mm}$, was washed by ultrasonic cleaner with trichloroethylene and deionized water before treatment.

The discharge apparatus was placed in the atmosphere, and the discharge area was purged with $\text{H}_2/\text{He}$ mixture gas. The upstream plasma for diborane generation and downstream plasma for PTFE treatment were generated with a 27.12 MHz and 300 kHz power supply, respectively. Table 1 shows the plasma treatment conditions. Treated PTFE sheets were examined using XPS, water contact angle (WCA) measurement and paint abrasion test.

The chemical state was measured with the XPS (ULVAC-Phi, ESCA-5800ci). The X-ray source provides monochromatized Al Kα radiation at a power of 350 W. The takeoff angle used in these experiments is 45°. The binding energies of XPS spectra were corrected with the $\text{C}_{1s}$ peak position (C-C, 284.6 eV) and the $\text{F}_{1s}$ peak position (PTFE, 689.0 eV) [10, 11].

The water contact angle measurement was carried out as follows: a treated sample was laid on a level plane and $1 \mu\text{L}$ of diluted water was dropped on its surface. Then the angle was measured with a goniometer. The value of the contact angle was the average of angles measured at 5 points on the sample.

The samples for the peel test were prepared in the following way. First, a treated PTFE sheet was glued on an aluminum plate with an epoxy glue (Ciba-Geigy Co., Ltd., Araldite). Then, it was pressed and kept at $50 ^\circ\text{C}$ for 12 hours.

| Discharge power of diborane generation | 500 W |
| Discharge power of PTFE treatment | 50 W |
| Treatment time | 0.5 ~ 5 min |
| He flow rate | 2 slm |
| H₂ flow rate | 10 sccm |
| O₂ flow rate | 5 sccm |
| Pressure | atmospheric pressure |

Table 1 The plasma treatment conditions.

Fig. 1 Schematic diagram of the discharge apparatus.
When the adhesive strength was measured, the peel speed was fixed at 200 mm min⁻¹. A PTFE sheet treated with a surfactant (NILACO Co., Ltd., Tetra Etch) was used as a control sample: this sheet was soaked in the surfactant for 10 seconds, and then it was rinsed with ethanol and diluted water.

3. Results and discussions

Fig. 2 and 3 show the variation of the WCA and the atomic content ratios calculated from XPS results of the diborane/H₂/He plasma treated PTFE, respectively. The WCA values became lower WCA as increasing the plasma treatment time. Meanwhile, the O/C values of the treated PTFE were quite low as show in Fig. 3. This result suggested that the chemical state of the treated PTFE surface came close to that of polyethylene because of the defluorination of PTFE and the additional reaction of hydrogen atoms. According to the WCA of a general polyethylene film (about 80°), the reason of the low WAC (about 40°) was supposed that the surface morphology of the treated PTFE became rougher [6]. Though the fluorine atoms on the treated PTFE surface were not removed completely, the F/C value was decreased to about twentieth of that of untreated PTFE and was lower than that of a PTFE treated by the H₂/He plasma (without diborane, F/C ≈ 0.4).

Next, the adhesive strength between treated PTFE and epoxy glue was examined. Fig. 4 shows the variation of the adhesive strength. The adhesive strength became stronger linearly as increasing the treatment time. And those treated more than 2 minutes showed higher values than that of control PTFE. The adhesive strength of 5 minutes treated PTFE was about twice as much as that of control PTFE, and it was high enough adhesive strength for practical use. However, since more high adhesive strength is required in some cases, the introduction of oxygen functional groups into the diborane/H₂/He plasma treated PTFE surface was investigated.

At first, PTFE was treated by the diborane/H₂/He plasma for 5 minutes, and then this PTFE was treated by the O₂/He plasma in addition. Fig. 5 shows the variation of the adhesive strength of the O₂/He plasma treated PTFE as a function of the O₂/He plasma treatment time. As shown in Fig. 5, this plasma treatment indicated unexpected
result: the adhesive strength was decreased by the O_{2}/He plasma. To investigate the cause of this result, the chemical state of those PTFE sheet surfaces were examined via XPS measurement.

The C\textsubscript{1s} XPS spectra were shown in Fig. 6. Although the peak assigned the CF\textsubscript{2} group in the C\textsubscript{1s} XPS spectrum of the diborane/H\textsubscript{2}/He plasma treated PTFE became smaller than that of untreated PTFE, the C\textsubscript{1s} spectrum of the O\textsubscript{2}/He plasma treated PTFE was the same as that of untreated PTFE. To investigate the cause of this result, angle resolved XPS measurement of diborane/H\textsubscript{2}/He plasma treated PTFE (5 min) was performed. As shown in Fig. 7, F/C decreased as decreasing the takeoff angle. And the intensity of CF\textsubscript{2} peak shown in Fig. 8 was increased as decreasing the takeoff angle: the defluorinated layer thickness was estimated 10 ~ 20 nm. Therefore, it was considered that the defluorinated layer on the diborane/H\textsubscript{2}/He plasma treated PTFE was ashed and removed by the O\textsubscript{2}/He plasma treatment since this layer thickness was quite thin.

4. Conclusion

The improvement of PTFE adhesiveness was succeeded by the defluorination treatment with

![Graph](image1)

Fig. 5 The variation of the adhesive strength as a function of the O\textsubscript{2}/He plasma treatment time.

![Graph](image2)

Fig. 6 The C\textsubscript{1s} XPS spectra of a) untreated, b) diborane/H\textsubscript{2}/He plasma treated and c) O\textsubscript{2}/He plasma treated PTFE. The treatment times of b) and c) were 5 min and 30 s, respectively.
the diborane generation plasma. To obtain stronger adhesiveness, it is needed to consider this plasma treatment process for much thicker defluorinated layer.

References