Defluorination Treatment of Polytetrafluoroethylene by B_2H_6 /He Plasma at Atmospheric Pressure

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B_2H_6 /He plasma and B_2H_6 /H₂/He plasma treatments of PTFE were performed. Concentration of the B_2H_6 was varied through this experiment. Then defluorination degree and adhesive strength were measured. While B_2H_6 and hydrogen were effective for defluorination of PTFE surface, oxygen functional groups generated by post-oxidation improved adhesive strength. The atmospheric pressure glow plasma treatment with lower diborane concentration more modifies PTFE surface.

Keywords: polytetrafluoroethylene, surface treatment, atmospheric pressure glow plasma, defluorination, adhesion improvement

1. Introduction

Fluorinated polymers have taken an important role in industry development. The most typical fluorinated polymer, polytetrafluoroethylene (PTFE) has specific characteristics: high heat resistance, high chemical resistance, low coefficient of friction, high insulation, etc. Thus, PTFE is used for chemical plants, coating electric wires or cookware. However, PTFE's application is limited because of its poor adhesion. Although agents containing metallic sodium are used as a solution of this problem currently, this treatment needs a large amount of washing water and produces much waste liquid. Besides, the treatment turns the treated surface into blackish. Therefore, a new dry process is expected instead of the wet treatment.

The atmospheric pressure glow (APG) plasma treatment is the most effective alternate method because of the high density of excited species, low temperature and uniform surface treatment [1-3].

In our previous studies, APG plasma treatments with boron compounds were performed for defluorination and adhesive improvement of

PTFE surface. Gaseous boron compounds were generated from a boron plate performed H₂ plasma treatment, then boron compounds, hydrogen and helium mixture gas was used for the treatments. According to our consideration, fluorine atoms separated from PTFE surface were bonded with boron atoms, then they became boron trifluoride (BF₃). This leads to effective defluorination. In consequence, almost complete defluorination and great adhesion improvement were attained [4-5]. However, it was not identified what kind of boron compound was generated and its concentration was unknown.

In this study, diborane (B_2H_6) was used as one of boron compounds, and the B_2H_6 concentration effect on the defluorination and adhesive improvement was investigated via B_2H_6 /He plasma and B_2H_6 /H₂/He plasma treatments.

2. Experimental

Fig. 1 shows the standard dielectric barrier discharge chamber with the shower head electrode. The dimension of PTFE sheet is 20 mm × 50 mm × 0.2 mm, and it was washed with

trichloroethylene and deionized water in a ultrasonic cleaner before treatment. A PTFE film was put on the power electrode. A rotary pump first evacuated the chamber, and then the pressure was restored with $B_2H_6/(H_2)/He$ mixture gas at atmospheric pressure. The plasma was generated with a 13.56 MHz power supply. Table 1 shows the plasma treatment conditions. B_2H_6 flow rate is equals to a ratio of B_2H_6 to helium.

The chemical state was measured with the XPS (ULVAC-Phi, Versa Probe II). The X-ray source provided monochromatized Al $K\alpha$ radiation at a power of 25 W. The takeoff angle was 45° . The binding energies of XPS spectra were corrected with the C_{1s} peak position (C-C, 284.6 eV) [6-7].

The samples for the peel test were prepared as follows: first, a treated PTFE sheet was glued on an stainless steel plate with an epoxy glue (NICHIBAN Inc. Araldite), and was pressed for 24 hours. The adhesive strength was measured by 180° peel tester at 200 mm min^{-1} peel speed.

3. Results and discussions

Before the B_2H_6 effect was investigated, suitable discharge power and treatment time were determined. Fig. 2 shows a relation between atomic ratio F/C obtained from XPS and discharge power of B_2H_6/He plasma treatments. In spite of increasing the discharge power, there was little difference in F/C. Thus, the discharge power was fixed at 100 W because of the smallest heat effect. Fig. 3 shows a relation between F/C and treatment time of B_2H_6/He plasma treatments. The F/C value decreased immediately at 0.5 min treatment time. And treated PTFEs showed almost same F/C values. Thus, treatment time was fixed at 5 min for plenty time.

Next, we examined the effect of B_2H_6 concentration. Fig. 4 shows relation between F/C and B_2H_6 concentration of B_2H_6/He plasma and $B_2H_6/H_2/He$ plasma treatments. While F/C values of the B_2H_6/He plasma did not depend on the B_2H_6 concentration, those of the $B_2H_6/H_2/He$ plasma increased as the B_2H_6 concentration increasing. As a result, the $B_2H_6/H_2/He$ plasma treatment of lower B_2H_6 concentration was effected the defluorination. In a case of 1000 ppm, white powder appeared and covered the PTFE surface. It was identified as

Fig. 1 Schematic diagram of the discharge chamber.

Table 1 The plasma treatment conditions.

Discharge frequency	13.56 MHz
Discharge power	100 ~ 200 W
Discharge gap	3 mm
Treatment time	0.5 ~ 20 min
He flow rate	2 slm
H_2 flow rate	6 sccm
B_2H_6 flow rate	0~1000ppm (0~2sccm)

Fig. 2 The relation between F/C and discharge power (treatment time: 5 min, B_2H_6 : 10 ppm)

compounds including B-O and B-B bonds by XPS measurements.

Fig. 5 shows relation between adhesive strength and B_2H_6 concentration of B_2H_6/He plasma and $B_2H_6/H_2/He$ plasma treatments. While adhesive strength values of the B_2H_6/He plasma decreased as the B_2H_6 concentration increasing, those of the $B_2H_6/H_2/He$ plasma showed almost same adhesive strength. Fig. 4 and 5 show that there is no relation between F/C and adhesive strength.

In order to examine the reasons for the above results, C1s spectra of XPS were investigated as shown in Fig. 6 and 7. The spectra were divided into C-C, C-O, C=O, CF, CF_2 peaks. CF_2 peak area decreased and C-C peak one was increased by the defluorination process. It was considered that defluorination changed the PTFE surface to polyethylene like surface. We focused attention on oxygen functional groups (C-O, C=O) because only defluorination might not able to attain such adhesion improvement up to about 700 Nm^{-1} . It is well known fact that oxygen functional groups increase adhesive strength between polymer and glue.

Fig. 8 shows variation of an area ratio of C-O and C=O peaks ($S_{C-O, C=O}/S_{all}$). Fig. 9 shows relation between O/C and B_2H_6 concentration. Since O/C of 100 ppm in $B_2H_6/H_2/He$ plasma was about 5.0 because of powder generation, this result is not indicated in Fig.9. In the B_2H_6/He plasma treatment, C-O and C=O peak areas decreased as the B_2H_6 concentration increasing. On the other hand, those of $B_2H_6/H_2/He$ plasma treatment kept small values. These tendencies corresponded to those of adhesive strength. Therefore, the oxygen functional groups improved the adhesive strength.

We considered the reactions on the PTFE surface as follows: metastable helium atoms generated by the plasma divided C-F bonds. After that, radical site was generated on carbon atoms. If this surface was exposed to the air, the radical site and oxygen in air reacted (post-oxidation). It was the reason why C-O and C=O peaks existed in Fig. 6 and 7. At the same time, B_2H_6 and hydrogen separated into boron and hydrogen atoms. They might involve defluorination combining with fluorine atoms separated from PTFE and becoming boron trifluoride (BF_3) and hydrogen fluoride (HF). However, hydrogen atoms also combined with the

Fig. 3 The relation between F/C and treatment time (discharge power: 100 W, B_2H_6 : 10 ppm)

Fig. 4 The relation between F/C and B_2H_6 concentration (discharge power: 100 W, treatment time: 5 min)

Fig. 5 The relation between adhesive strength and B_2H_6 concentration (discharge power: 100 W, treatment time: 5 min)

Fig. 6 C1s spectra of the B₂H₆/He plasma treatment

Fig. 7 C1s spectra of the B₂H₆/He plasma treatments

radical site (additional reaction). Indeed hydrogen atoms contributed to defluorination; however, they prevented post-oxidation due to the additional reaction. Therefore, the C-O and C=O peak areas and the adhesive strength of the B₂H₆/He plasma decreased as B₂H₆ concentration increasing. The B₂H₆/H₂/He plasma treatments gave little C-O and C=O peak areas and adhesion improvement to the PTFE surface because of a large amount of

Fig. 8 The relation between the ratio of C-O and C=O peak areas to the total peak area and B₂H₆ concentration (discharge power: 100 W, treatment time: 5 min)

Fig. 9 The relation between O/C and B₂H₆ concentration (discharge power: 100 W, treatment time: 5 min)

hydrogen atoms encumbering post-oxidation.

In this study, a maximum adhesive strength was obtained at the He plasma treatment (the B₂H₆/He plasma treatment at 0 ppm). However, He plasma treatments showed little adhesion improvement in our previous study [8]. And according to another previous study of plasma treatments with boron compounds, it is considered that only a few boron compounds were generated in the plasma zone since there was no change on the boron plate surface [5]. Therefore, we guessed that a treatment of quite low B₂H₆ concentration is effective for PTFE modification.

4. Conclusion

B₂H₆/He plasma and B₂H₆/H₂/He plasma treatments in the case of B₂H₆ concentration of 1000 ppm or less were performed. It seems that while B₂H₆ and hydrogen contribute to defluorination, post-oxidation concerns adhesion improvement. It is considered that treatments with lower B₂H₆ concentration more modifies PTFE surface.

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