Surface Treatment of Fluorinated Polymers using Atmospheric Pressure Glow Discharge System

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During the past decade, we have examined the surface improvement of PVF, FEP, PFA, and PTFE films by APGD system. Their adhesive strength with an epoxy resin could be improved that attained by different kind gas introduction to the plasma system. Last year, new idea using $\text{NH}_4/\text{H}_2\text{O}$ as the treating gas was proposed in the low pressure glow discharge (LPD) to treat PTFE by T. Yajima et al. So we examined the surface effects in both process, APGD and LPD, using $\text{NH}_4/\text{H}_2\text{O}$ mixture. APGD treatment could not have any chemical effect on the PTFE surface. On the other hand, LPD, we got the proof of super hydrophilicity on the PTFE. It seemed that in the low pressure, a slow sputtering will be a preceding reaction on the PTFE even used the $\text{NH}_4/\text{H}_2\text{O}$. The difference of the kinetics was considered in the evaluation of both processes, APGD and LPD.

Keywords: fluorinated polymers, surface treatment, atmospheric pressure glow discharge, low pressure discharge, sputtering

1. Introduction

Fluorinated polymers such as poly vinyl fluoride (PVF), tetrafluoroethylene hexafluoropropylene copolymer (FEP), tetrafluoroethylene perfluoro alkylvinylether copolymer (PFA), and polytetrafluoroethylene (PTFE) have many unique characteristics, for example, high chemical resistance, high heat resistance, low coefficient of friction and so on. Thus, they have been used as typical inert materials for many hard situations. Nevertheless, they have problems such as difficulty of adhesion and hydrophobic nature. In general, fluorinated polymers cannot treat with a convenient process such as corona discharges, because they can add only low effects to the chemically inert surfaces. Some agent, which contain metal sodium, are usually used to add the adhesibility or the hydrophilicity to the fluorinated polymers. However, this treatment needs a large amount of cleaning water and thus the disposal of much waste fluid. Moreover, the treated surfaces become blackish. From the reason, a new dry process had been desired instead of the wet treatments. Several

studies of the surface treatment with low-pressure glow discharge (LPD) were reported [1,2]. However, this method has not been widely used for industry because of the low through put and difficulty of applying it to an assembly line directly.

The atmospheric pressure glow discharge (APGD) can generate spatially uniform plasma even at atmospheric pressure if only one uses a high frequency generator of higher than 1 kHz, electrodes whose surfaces are covered with dielectric plates and a sample gas diluted with a large amount of helium gas [3-5]. By using of the atmospheric pressure, APGD is more suitable system to the industry than that of using low pressure discharge.

At first, we will examine three fluorinated polymers (PVF, FEP and PFA) other than PTFE. The changes of their adhesion strength and chemical states measured by XPS will be shown.

In the case of PTFE, it has only- CF_2 bonds that is surrounded on the strait carbon chain. From the reason, it is most difficult substance to eliminate the fluorine atom from the carbon chain.

So, we needed to use a different system and gas to treat PTFE [6] other than those above tree fluoropolymers.

At final, we will try to compare the APGD and the LPD [7] in which is better plasma system for the PTFE treatment.

2. Experimental

2.1. Treatment of PVDF, FEP and PFA in APGD using normal gas

In the case of the treatment for three polymers, PVF, FEP, PFA, we used parallel plate electrode (diameter: 125 mm, the gap length: 2 mm, 1 atm) discharge system, that stored in a glass chamber. The plasma was generated with a 100 kHz power supply at 50 W. Treatment mixture gases were O₂, N₂, and Ar gases diluted with large amounts of He or He alone. The flow rates of gas mixture were as follows, He: 2 slm, and O₂, N₂, Ar were each 5 sccm. A rotary pump first evacuated the chamber and the pressure was then restored with a treatment mixture gas at atmospheric pressure. Treatment time was 0.5~5 min. Polymer sample (NILACO Co. Ltd., 0.05 mm films, sizes: 20×40 mm) was placed on the lower electrode that connected with the ground. Water contact angle (CA) was measured using contact angle meter. A treated sample film was glued on an aluminum plate with epoxy glue. The peel test was obtained by 180deg. peele tester (HEIDON-14). XPS (ULVAC-Phi, ESCA5800ci) was used for the surface analysis. The details of the schematics were shown in reference [6].

2.2. Treatment of PTFE in APGD with diborane-plasma system

Boron trifluoride (BF₃) is the gaseous fluorine compounds at room temperature and the bond enthalpy of fluorine with boron (757 kJ mol⁻¹) is much bigger than that of fluorine with hydrogen or carbon (570 or 552 kJ mol⁻¹) [8]. It seemed that the defluorination of PTFE will be possible with using diborane (B₂H₆) dissociation plasma.

Fig. 1 shows the discharge apparatus which have two discharge areas [9]. The discharge areas were bounded for quartz glass plates, and so H₂/He mixture gas flowed in one direction. The upstream and downstream discharge areas were used for diborane generation and PTFE surface treatment,

Fig. 1. Schematic diagram of diborane/H₂/He-APGD system.

respectively. The boron plate (thickness, about 0.1 mm) was prepared by solidification of boron powder (0.3 g) with inorganic adhesive (0.3 g, Aron Alpha Inc., Aron Ceramic D). PTFE sheet, whose sizes were 20 mm × 20 mm × 0.2 mm.

The treated sample surface was evaluated as same as in the 2.1. Discharge power for diborane generation was 27.12 MHz, 500 W, and for diborane dissociation plasma was 300 kHz, 50 W. The flow rates of gas mixture were as follows, He: 2s lm, H₂: 10 sccm. Treatment time was 0.5~5 min.

2.3. Treatment of PTFE with NH₃-H₂O/He in LPD and APGD systems

RF (13.56 MHz, 100 W) discharge and parallel electrodes were used in the both plasma systems as same as in the 2.1. The electrode gaps were 15 mm for low pressure (0.6 Torr) system and 2 mm for APG (1 atm) system respectively. The sample film (PTFE, 0.5 mm × 2 cm × 3 cm) was placed on the grounded electrode. Sample gas was introduced to the chamber path troughed the bubbling system of NH₃ (10%) aqueous solution with 10 sccm of He flow. The sample gas conditions were followed with in the reference [7]. In the case of the APGD, NH₃+H₂O (10%) vapor with 10 sccm of He flow that was diluted by 2 slm of He.

3. Results and discussion

3.1. PVF, FEP and PFA treatments in APGD

Figure 2 a ~ c show the variation of the atom composition ratios of F/C and O/C+N/C calculated from XPS measurement. Fig. 2a shows the untreated PVF and they were slightly oxidized. The variation of F/C shows the reduction of fluorine atoms. And O/C+N/C show some

Fig. 2. The variation of the atom number ratios of F/C and O/C+N/C observed from XPS. Sub-figures (a), (b) and (c) are the results of PVF, FEP and PFA, respectively. Treatment gases were —■— He,○..... O₂/He, -◇- N₂/He and -▲- Ar/He.

additional atoms due to the plasma treatments. In the case of PVF, the ratios of O/C+N/C were saturated for a short time treatment. We assumed that PVF had only one fluorine atom in its unit structure and that PVF was oxidized more easily than other fluorinated polymers. On the other hand, the ratios of O/C+N/C of FEP and PFA increased as the treatment time increased. Especially, those of He plasma-treated samples increased significantly and the ratios of F/C decreased simultaneously. All the results of O₂/He plasma treatment showed relatively low ratios of O/C+N/C

and high ratios of F/C. It seemed that O atom has lower reactivity than other kind of atoms on the fluorinated polymers. Figure 3 shows adhesive strength of FEP and PFA treated in APGD.

The peel force of plasma-treated PVF could not be measured because their adhesive strength was beyond the value of the measurement instrument limit ($2.00 \text{ kg} \cdot 20 \text{ mm}^{-1}$). Moreover, it was higher than that of the target level, whose peel force was $1.06 \text{ kg} \cdot 20 \text{ mm}^{-1}$. The adhesive strength of FEP and PFA treated by plasma were approximately 180 and 80 times stronger than that

Fig. 3. The variation of the peel force. Sub-figures (a) and (b) are the results of FEP and PFA, respectively. Treatment gases were —■— He, —■— O₂/He, —■— N₂/He and -▲- Ar/He.

Fig. 4. The variation of the atomic content ratios F/C (●) and O/C (□) as a function of the treatment time on the diborane/H₂/He plasma treated PTFE.

of the untreated films, whose peel forces were 0.4 and 0.6 kg·20 mm⁻¹. In addition, the results of FEP showed the higher force values than the target level, while those of PFA showed slightly lower than that of the target level. For the treatment of PFA, further harder system will be needed, because PFA has not hydrogen in the structure.

3.2. Treatment of PTFE in APGD with diborane/H₂/He plasma system

Fig. 4 shows the variation of the atomic content ratios of F/C and O/C calculated from XPS results of the diborane/H₂/He plasma (Boron-APGD) treated PTFE. The O/C values of the treated PTFE were quite low as shown in Figure 4. This result suggested that the chemical state of the treated PTFE surface came close to that of polyethylene because of defluorination of PTFE and additional reaction of hydrogen atoms. It is certain that the surface morphology of the treated PTFE became rougher [9] that provides the increasing of the adhesive strength. 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.

Next, the adhesive strength between treated PTFE and epoxy glue was examined. Figure 5 shows the variation of the adhesive strength (peel force: 1

kgf 20 mm⁻¹ ≈ adhesive strength: 4.9×10^2 Nm⁻¹). The adhesive strength became stronger linearly as increasing the treatment time [9]. And those treated longer than 2 minutes showed higher values than that of target value. The adhesive strength of 5 minutes treated PTFE was about twice as higher as that of target value, and it was high enough adhesive strength for practical use.

Fig. 5. The variation of the adhesive strength as a function of the treatment time. The dashed line shows the control sample value.

3.3. Treatment of PTFE with NH₃-H₂O/He in LPD and in APGD systems

For a reaffirmation, a comparative study has been done with the LPD and APGD systems.

Fig. 6 shows the surface wettability of PTFE as a changing of the treated time in LPD and APGD. When we use LPD with NH₃-H₂O/He, water contact angle was decreased with increasing of the elapse time. In the longer treating time than 30 minutes, CA was going to lower than 5 degree. Thus, the appearance of the super hydrophilicity on the PTFE surface which was shown in the reference [7] has been demonstrated. On the PTFE treated with NH₃-H₂O/He in LPD system, O1s or N1s spectra were found that for certain assigned as carboxyl or amide group which was measured by XPS (not shown). Normally, an electro negativity of the carboxyl group is enhanced by containing of amide group that arise the enhancement of hydrophilicity in the molecule. This is one of the

reasons why we see the super hydrophilicity at longer treatment time of PTFE in LPD in figure 6. In contrary, in the APGD, the CA shows almost no change with changing of the elapse time even using the same gas composition and discharge power, except of the operating pressure. It is well known that some kinds of radicals cannot easy react with PTFE such as O atom, H atom, OH and

Fig. 6. Water contact angle θ as a function of treatment times of PTFE that treated in LPG (0.6 Torr) and $\text{NH}_3\text{-H}_2\text{O/He}$ APG discharge (1 atm).

NH_n . Because, $-\text{CF}_2$ bond is too strong to react with such radicals. So, in LPD, some supporting reaction should be expected as sputtering reaction to enhance the radical reaction on the PTFE in LPD [10]. The adhesive strength which treated in APGD with $\text{NH}_3\text{-H}_2\text{O/He}$ was the same as that of the untreated PTFE. Figure 7 shows the adhesive strength which treated in LPD with $\text{NH}_3\text{-H}_2\text{O/He}$. In the figure, also shows the surface treated in the Boron-APGD system [11]. In the LPD treated surfaces, $\text{H}_2\text{O/He}$ system shows faster increasing rate than that of $\text{NH}_3\text{-H}_2\text{O/He}$, but it shows much slower rate than that of the treated in Boron-APGD system. Suppose the rate determining step will be attributed to the slow sputtering reaction on the PTFE even in the $\text{NH}_3\text{-H}_2\text{O/He}$ LPD. On the other hand, at the Boron-APGD system, reactive metallic boron produced in APGD directly extracts the fluorine atom from $-\text{CF}_2$ bond of PTFE and then post oxidation will be occurred by the exposing in the air. In the case of PFA, also it could attain good adhesibility with boron-APGD system [6].

4. Conclusion

Fig. 7. The adhesive strength with epoxy adhesion as a function of treatment times treated in LPD and Boron-APGD with variation of treating gas.

For PVD and FEP, they are relatively easy to obtain good adhesibility with O_2 , N_2 , Ar in He or He only in APGD. In the PFA and PTFE, from the reason of the perfluorinated polymers, Boron-APGD is better system than that of the $\text{NH}_3\text{-H}_2\text{O/He}$ LPD to refine the surface adhesion strength.

References

1. T. Hirotsu and S. Ohnishi, *J. Adhesion*, **11** (1980) 57.
2. J. P. Badey, E. Espuche, Y. Jugnet, B. Chabert and T. M. Duc, *Int. J. Adhes. Adhes.*, **16** (1996) 173.
3. S. Kanazawa, M. Kogoma, T. Moriwaki and S. Okazaki, *J. Phys. D*, **21**, 838 (1988).
4. T. Yokoyama, M. Kogoma, T. Moriwaki and S. Okazaki, *J. Phys. D*, **23**, 1125 (1990).
5. T. Yokoyama, M. Kogoma, S. Kanazawa, T. Moriwaki and S. Okazaki, *J. Phys. D*, **23**, 374 (1990).
6. K. Tanaka, T. Inomata and M. Kogoma, *Thin Solid Films*, **386**, 217 (2001).
7. H. Wenfeng, H. Tei, K. Shimizu, and T. Yajima, 32nd ICPST-B2-12.
8. D. R. Lide (ed.), *Handbook of Chemistry and Physics*, 81st edition, CRC Press, USA (2000).
9. K. Tanaka and M. Kogoma, *Int. J. Adhes. Adhes.*, **23** (2003) 515.
10. J. M. Tibbit, M. Shen, and A. T. Bell, *Thin Solid Films*, **29** (1984) L43.
11. M. Kogoma, K. Takahashi and K. Tanaka, *J. Photopolym. Sci. Technol.*, **24** (2011) 441.