Surface Modification of Polytetrafluoroethylene by Line Shaped Ar/Ethanol Atmospheric Pressure Plasma Jet

H. Yajima¹, I. Serizawa¹, H. Furuta², and A. Hatta²

¹ ORC Manufacturing Co. Ltd., 4896 Tamagawa, Chino, Nagano 391-0011, Japan
² Kochi University of Technology, 185 Miyawatani, Tosayamada, Kami, Kochi 782-8502, Japan
Email: h-yajima@orc.co.jp

By using line shaped atmospheric pressure plasma jet (APPJ) of Ar with ethanol vapor, the wettability of polytetrafluoroethylene (PTFE) surface was improved. After plasma treatment for 10 minutes, hydrophilic surface of 42° water contact angle was achieved while the original surface showed 113°. It was found that Hydrogen molecules were produced from ethanol in the APPJ.

1 Introduction
For variety of industrial application of polytetrafluoroethylene (PTFE), it is required to improve the surface property of poor adhesion with other materials. Plasma surface treatments have been expected to modify the PTFE surface and some successful results have been reported. Atmospheric pressure plasma techniques have many advantages for treatment of polymer surface; no usage of vacuum system, simple configuration of apparatus, high density plasma for rapid treatment, small environmental impact, and so on.

We previously reported surface modification of PTFE by atmospheric pressure plasma using mixture gas of Ar and ethanol vapor with parallel plate electrodes configuration [1]. Due to the configuration, however, the treatment is limited for thin sheet of PTFE set between the electrodes for dielectric barrier discharge (DBD). For treatment of thick material with variety of shapes, irradiation to atmospheric pressure plasma jet (APPJ) will be effective. For such the surface treatment, we have been developing a line shaped DBD-APPJ device which can eject line shaped plasma plume instead of the pencil type APPJ [2].

In this study, we examined surface modification of PTFE by the line shaped Ar/ethanol DBD-APPJ. The hydrophilicity of treated PTFE was evaluated and the chemical component in gas jet was analyzed using quadrupole mass spectroscopy (QMS).

2 Experimental setup
Figure 1 shows experimental setup of PTFE surface modification and APPJ configuration. Ar gas was bubbled in ethanol in a bottle for supplying the ethanol vapor and the mixture gas was fed into the discharge gap. Ar gas was supplied at a flow rate of 500 sccm and the mixing ratio of ethanol vapor to Ar gas was 5.7 % by controlling the ethanol temperature at 20 °C. A DBD was operated in a small gap between a pair of glass plates with a pair of electrodes stuck on both the outsides of the glass plates, and a 25 kHz sinusoidal wave voltage at 10kVp-p was applied to the electrodes.

The sample of PTFE sheet was located at the exit of APPJ. Before plasma treatment, the samples were washed in an ultrasonic cleaning instrument by using acetone for 5 min., and then, rinsed in ethanol and ultrapure water for each 5 min. Treated PTFE samples were characterized by the static water contact angle 30 seconds after dropping distilled water. The volume of water drop was around 1 µL.

Figure 2 shows experimental setup of QMS measurements. The tip of glass capillary was located just below 1 mm flow the exit of APPJ apparatus.

3 Results and Discussion
Figure 3 shows water drop images on PTFE untreated and treated with Ar or Ar/ethanol APPJ for 10 minutes.
at 1 mm irradiation distance. By using Ar/ethanol APPJ, hydrophilic surface of 42° water contact angle was achieved while the original surface showed 113°. As it has been reported that Ar plasma was effective for hydrophilic PTFE [3], the Ar APPJ treated PTFE also showed slightly decreased water contact angle 91°.

Figure 4 shows H$_2^+$ ($m/z$ = 2) current of QMS measurements at 1 mm distance from the APPJ exit with Ar or Ar/ethanol with plasma on and off. In the case of Ar/ethanol APPJ, hydrogen molecules were generated from decomposition of ethanol (C$_2$H$_5$OH). The production of hydrogen molecules implies possible existence of hydrogen radicals in the plasma jet. It can be assumed that C-F bonds of PTFE surface was decreased by attack of hydrogen radicals with resulting in the highly improved wettability [4].

Figure 5 shows dependency on the treatment time of the static water contact angle of treated PTFE surface with Ar/ethanol APPJ at 1 mm irradiation distance. The decrease of contact angle was saturated at around 42° in 10 minutes.

Figure 6 shows dependency of the static water contact angle on the irradiation distance from the exit of APPJ with Ar/ethanol for 10 minutes. It was confirmed that the irradiation was effective to improve the wettability below 5 mm distance.

The resulting improvement of wettability was not sufficient for a practical use, it is necessary to optimize the operation conditions of APPJ.

4 Conclusion

The hydrophilicity of PTFE treated by the line shaped DBD-APPJ device using Ar/ethanol gas was examined. After plasma treatment for 10 minutes, hydrophilic surface of 42° water contact angle was achieved while the original surface showed 113°. It can be assumed that C-F bonds of PTFE decreased by attack of hydrogen radicals generated from ethanol with resulting in the improved wettability.

References