

Effect of Monomer Concentration on Adhesive Strength of PTFE Film in Atmospheric Plasma Graft-Polymerization Process

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Abstract— The effect of monomer concentration on adhesive strength of polytetrafluoroethylene (PTFE) film in atmospheric pressure nonthermal plasma (NTP) graft-polymerization process is investigated. In the atmospheric pressure NTP graft-polymerization process, the atmospheric pressure NTP technique followed by the application of a graft polymerization layer of a hydrophilic monomer onto the polymer textiles and films is used. In this study, we use acrylic acid ($\text{CH}_2=\text{CHCOOH}$) as monomer. We prepare the two types of evaporation vessels for generating monomer vapor: vessel I and vessel II. Vessel II is a pair of evaporation vessels that have a half evaporation area of vessel I. When vessel I is used, it is placed at the front side of a conveyor belt. When vessel II is used, vessel II is placed at both sides of the conveyor belt. By controlling the monomer temperature, we change monomer concentration in the treatment chamber. After the purge, a NTP jet is applied to the PTFE film surface with an Ar flow rate of 40 L/min. The monomer concentration is calculated using the amount of evaporated monomer and the Ar flow rate of 50 L/min. After the treated PTFE films are adhered to the stainless steel plates using a double sided tape, 90° peeling tests are conducted. As a result, the peeling strength increases with the decrease of monomer concentration. When the temperature of acrylic acid of vessel II is set at 55 °C, the monomer concentration is 980 ppm and the maximum peeling strength, 4.85 N/mm, is obtained. In spite of the same monomer temperature (60°C), the peeling strength of treated PTFE using vessel II is higher than that using vessel I and its dispersion is smaller. This result is caused by the distribution of monomer concentration. Furthermore, information regarding the chemical bonding and elemental composition of the untreated and treated films is obtained by X-ray photoelectron spectroscopy (XPS) measurements and the morphologies of the graft-polymerization surfaces are observed using a scanning electron microscope (SEM).

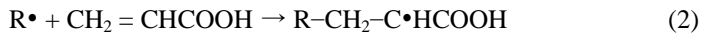
I. INTRODUCTION

Fluoropolymer films such as PTFE (polytetrafluoroethylene, $-\text{[CF}_2\text{-CF}_2\text{]}_n-$), PFA (perfluoroalkoxy fluoroplastics, $-\text{[CF}_2\text{-CF}_2\text{]}_n-\text{[CF}_2\text{-CF(OCF}_2\text{CF}_2\text{CF}_3\text{)]}_m-$), and

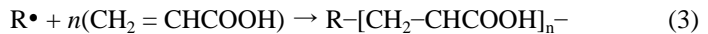
PCTFE (polychlorotrifluoroethylene, $-\text{[CF}_2-\text{CFCl]}_n-$) have excellent properties in terms of heat resistance, chemical resistance, electric insulation, flexibility, acting as gas barriers, incombustibility, electrical characteristics, and low friction. Therefore, it is expected to apply them to organic electroluminescence fluoropolymer film devices [1], medical devices such as endoscopes, medical machines, and flexible-tube-type medical syringes [2], and so on. However, it is difficult for fluorocarbon polymer films to adhere to other materials because their molecular structure is steady and inert. In order to adhere to other materials, surface treatment is necessary. As a conventional surface treatment, liquid-phase etching, via submersion in a sodium-ammonia solution, is often used [3]. However, this method has several drawbacks: bad processing environment, a large amount of effluent, the surface damage by the chemical etching process, and surface color change.

As an alternative method, a surface modification process of low-temperature nonthermal plasma (NTP) has been investigated [4]–[10]. Although NTP technologies that improve the surface properties of fibers and polymers have been used to enhance adhesion [4],[5] and hydrophilicity [6],[7], deepen color [8], and shrink-proof wooden fabrics [9], the effects on fluoropolymer films are not significant and do not last very long. In order to realize effective and permanent surface treatment, we had earlier proposed an atmospheric pressure NTP method followed by graft polymerization [11]–[15] of hydrophilic monomers such as acrylic acid ($\text{CH}_2=\text{CHCOOH}$). Polyacrylic films created by plasma graft polymerization are extremely stable against water or alcohol washing using an ultrasonic cleaner. This process is expressed as follows:

1) *NTP application*



2) *Graft polymerization*



where R represents the main chain composed of C, H, O, Cl, and F atoms in fluoropolymers, and $\text{R}\cdot$, $\text{F}\cdot$, and $\text{CH}_2\text{-C}\cdot\text{HCOOH}$ are the radicals.

The surface treatment of a PTFE film using atmospheric-pressure NTP graft polymerization was investigated, and copper plating on the treated PTFE films was achieved [16]. It is demonstrated that it is possible to bond A4-sized sheets of PTFE and metals without losing the excellent physical properties of PTFE [17], and photolithographic patterns are formed on the plated PTFE film [18]. In previous study, the influence of plasma torch cover on peeling strength and entrained flow near the torch were investigated to realize the stronger adhesion and better shape of the cover was determined [19].

In this study, the effect of monomer concentration on adhesive strength of PTFE film in atmospheric pressure NTP graft-polymerization process is investigated using the two types of evaporation vessels for generating monomer vapor. Furthermore, information regarding the chemical bonding and elemental composition of the untreated and treated films is obtained by X-ray photoelectron spectroscopy (XPS) measurements and the morphologies of the graft-polymerization surfaces are observed using a scanning electron microscope (SEM).

II. EXPERIMENTAL SETUP AND METHODS

A. NTP Treatment Equipment and Methods

Fig. 1 shows the experimental setup of NTP graft polymerization for the A4-sized fluoropolymer films. Industrial argon (purity = 99.99%) is used as a plasma gas. A grounded copper-laminated glass epoxy plate, which is covered with a PTFE film of 0.2 mm in thickness, is used as a sample holder and placed on a conveyer belt and moved in the longitudinal direction. A PTFE film (thickness = 0.2 mm, length = 290 mm, and width = 200 mm) is placed on the sample holder. NTP jets induced by gliding arc discharge at atmospheric pressure are applied to the surface. The entire PTFE film can be treated with this equipment.

The power supply system (PSC 1001, Pearl Kogyo Company, Ltd.) comprises a single plasma torch driven by a 20-kHz pulse-modulated ac power supply (pulse duty ratio = 99%, output voltage = 24 kV, pulse modulation frequency = 60 Hz, and average input power = 500 W). The distance between the surface of the sample film and the head of the plasma jet nozzle is fixed at 9 mm during the experiment. The two types of evaporation vessels are used for generating monomer vapor: vessel I and vessel II. Vessel I is a stainless-steel container (L 296 mm × W 38 mm × D 59 mm) filled with 200 g of acrylic acid monomer liquid (purity = 98 mass%, Wako Pure Chemical Industries, Ltd.) and is heated with a heater located under the container. Vessel II is a pair of evaporation vessels with 100 g of acrylic acid monomer liquid having a half width (19 mm) and the same length and depth of vessel I, namely, a half evaporation area of vessel I. When vessel I is used, it is placed at the front side of a conveyer belt. When vessel II is used, vessel II is placed at both sides of the conveyer belt. The temperature of the monomer is maintained constant at 60 and 55°C by a

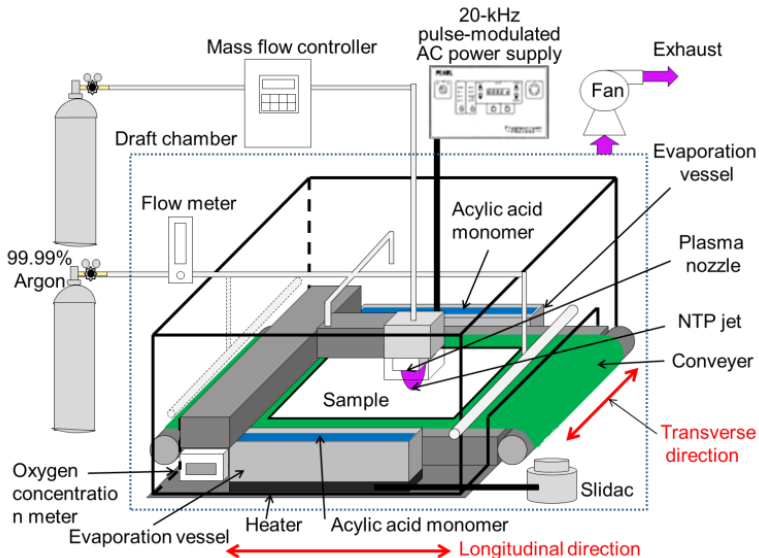


Fig. 1. Schematic diagram of experimental setup for atmospheric-pressure NTP graft-polymerization surface treatment of A4-sized fluoropolymer films.

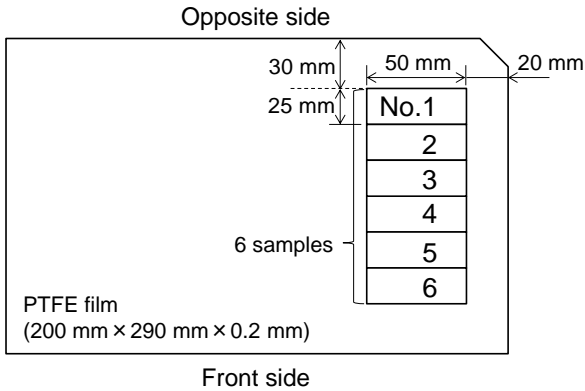


Fig. 2. Sample positions of treated PTFE film.

thermo controller. Because oxygen has a negative influence on the graft polymerization process, the treatment chamber (the volume is approximately 0.5 m^3) is purged with atmospheric-pressure Ar from 30 min before NTP treatment until the finish of the treatment. In addition, the gaps between the left and right aspects of the treatment chamber and a conveyer belt are covered with the brushes and Ar gas curtains in order to prevent an inflow of the outside air. The total flow rate of the purge and gas curtain is 20 L/min. After a purging duration of 30 min, a plasma jet is applied to the film surface with an Ar flow rate of 40 L/min. The plasma jet nozzle moves in the transverse direction at a velocity of 4 mm/s, and after the nozzle oscillates, it moves 1 cm in the longitudinal direction. The entire A4-sized region is treated continuously. The monomer concentration in the treatment chamber is calculated using the amount of evaporated monomer and a flow rate of Ar. After the plasma graft polymerization process, the treated films are cleaned in a bath filled with 1 L ethanol at 20°C for 10 min, and then dried for one day.

B. Evaluation Instrumentation and Methods

The PTFE films treated using the plasma graft polymerization apparatus are tested for adhesiveness. The six samples (thickness = 0.2 mm, length = 50 mm, and width = 25 mm) are cut from the treated PTFE film as shown in Fig. 2. The 90° peeling test—based on JIS No. K6854—after the double sided tape (KPS-25, 3M Company) is pasted on the surface of the tested PTFE samples (total length = 50 mm, pasted length = 30 mm, and width = 25 mm), the samples are stuck to a stainless steel plate (thickness = 1 mm, length = 50 mm, and width = 25 mm). The samples are held between steel plates, then kept for 24 h at a constant temperature (26°C). The 90° peeling strengths of adhered samples are tested using the 90° detachment testing equipment (Digital Force Gauge, maximum strength: 200 N, type: ZTA-200N, Imada Co., Ltd.). The sample width is 25 mm and the peeling speed is 100 mm/min. The time-dependent peeling force is recorded directly to the laptop computer. After the experiments data are processed. Information regarding the chemical bonding of untreated and treated films is obtained by XPS measurements using a spec-

trometer (ESCA5700, ULVAC-PHI, Ltd.). The morphologies of the graft-polymerized surfaces are observed with an SEM (S-4800, Hitachi High-Technologies Corporation).

III. RESULTS AND DISCUSSION

A. Peeling Strength

The peeling strength test for the untreated PTFE film was not performed because it was not stuck to a double sided tape. Fig. 3 shows the 90° peeling strength of the sample No.1 to 6 in the case of vessel I with the monomer temperature of 60°C . The monomer concentration was calculated at 1700 ppm. In this figure, the horizontal axis denotes the stroke and the vertical axis corresponds to the peeling strength per 1-mm-wide PTFE film. The peeling strength of sample No. 1 to 4 is stable in the range of 3.7 to 4.2 N/mm, while that of sample No.5 and 6 fluctuates. It is considered that this is caused by monomer concentration difference at sample position; that is, the monomer concentration at the sample positions of No.5 and 6, where is close to vessel I, becomes high.

Fig. 4 shows the peeling strength of the samples in the case of vessel II with the monomer temperature of 60°C . The monomer concentration was calculated at 1320 ppm. The number of treated PTFE film samples is six. The bold line and thin line represent mean value and standard deviation, respectively. From this figure, the mean value of peeling strength keeps around 4.4 N/mm and its standard deviation is small. It is considered that the non-uniformity of monomer concentration is improved by using vessel II.

Fig. 5 shows the peeling strength of the samples in the case of vessel II with the monomer temperature of 55°C . The monomer concentration was calculated at 980 ppm. The number of treated PTFE film samples is six. The mean value of peeling strength keeps around 4.9 N/mm and increases more than that of 60°C with keeping the standard devia-

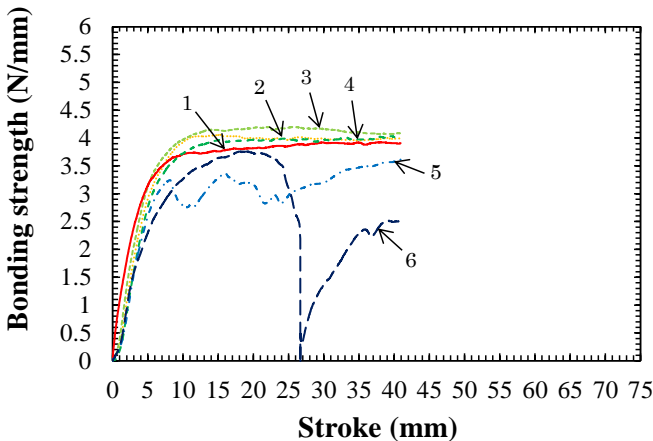


Fig. 3. Peeling strength of treated PTFE (vessel I, acrylic acid temperature 60°C).

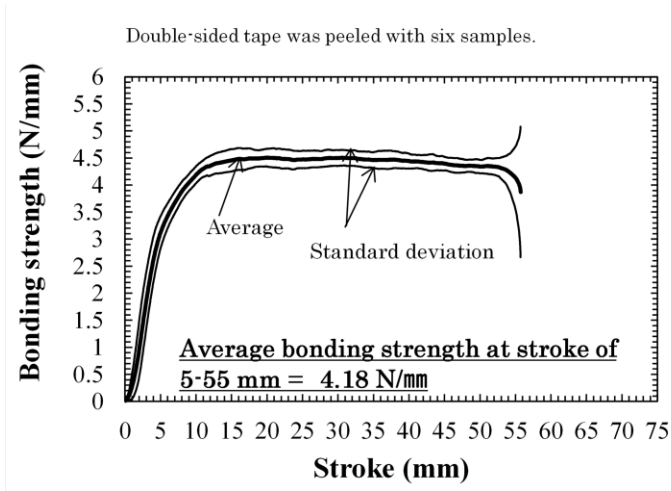


Fig. 4. Peeling strength of treated PTFE (vessel II, acrylic acid temperature 60°C).

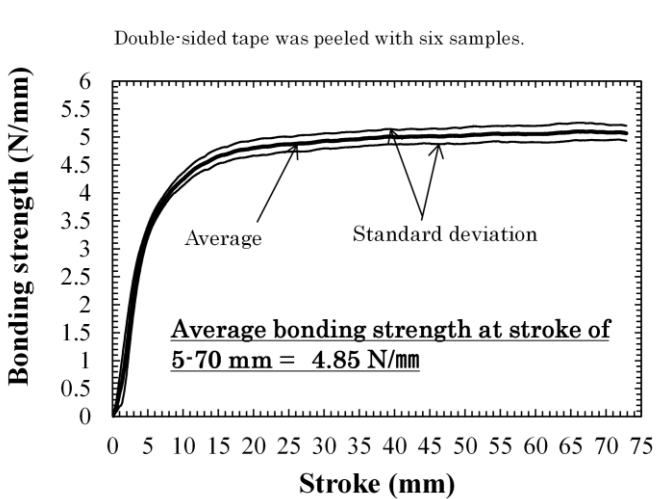


Fig. 5. Peeling strength of treated PTFE (vessel II, acrylic acid temperature 55°C).

tion small. From Figs. 3 to 5, the average peeling strength becomes higher when monomer concentration is lower. Moreover, the standard deviation becomes small by using vessel II.

B. XPS Analysis

The XPS analysis for the untreated PTFE film was performed [19]. The peak for $-\text{CF}_2-$ (difluoromethylene group), which is the origin of the film's hydrophobicity, was detected at 292 eV from the decomposition of the total C_{1s} spectrum.

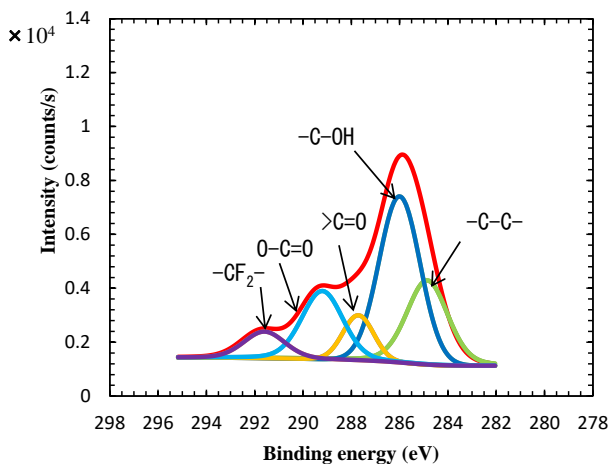


Fig. 6. XPS spectra of the C_{1s} peak for the surface of the PTFE film (vessel II, acrylic acid temperature 60°C).

Fig. 6 shows the C_{1s} XPS spectrum for the treated PTFE film in the case of vessel II with the monomer temperature of 60°C . Although $-\text{CF}_2-$ is detected, it is much smaller than that for untreated one. The peaks for $\text{O}-\text{C}=\text{O}$ (carboxyl group), $>\text{C}=\text{O}$ (carbonyl group), $-\text{C}-\text{OH}$ (alcohol), and $-\text{C}-\text{C}-$ (carbon) are detected at approximately 292, 288.8, 287.8, 286, and 284.4 eV, respectively, from the decomposition of the total C_{1s} peak. In general, surface adhesion is improved when hydrophilic functional groups such as carboxyl, carbonyl groups, and alcohol are attached to the polymer surface.

C. SEM Observation

Figs. 7(a) and (b) show the surface of the untreated and treated PTFE films. For the SEM results, each sample is observed at a magnification of 50,000, with a scale bar of $1.00\ \mu\text{m}$ representing 10 scales. As shown in Fig. 7 (a), an untreated surface of PTFE seems to be smooth. According to Fig. 7 (b), it can be confirmed that acrylic acid polymer is constituted by treatment. Each sample has polymers of less than $0.5\ \mu\text{m}$ diameter. At treated sample, polymer has reflected clearly in white and PTFE surface of the untreated portion can be partially observed. Although in our previous report [2], [18] almost whole region is covered by the polymer, the distribution of acrylic acid polymer is intermittent and makes the surface area increase. It is known from the results that appropriate amounts of polymerization could cause the increase in the peeling strength.

IV. CONCLUSION

The effect of monomer concentration on adhesive strength of PTFE film in atmospheric pressure NTP graft-polymerization process is investigated. As the monomer concentration decreases, the peeling strength becomes higher under the experimental conditions. In addition, the standard deviation becomes small by using vessel II.

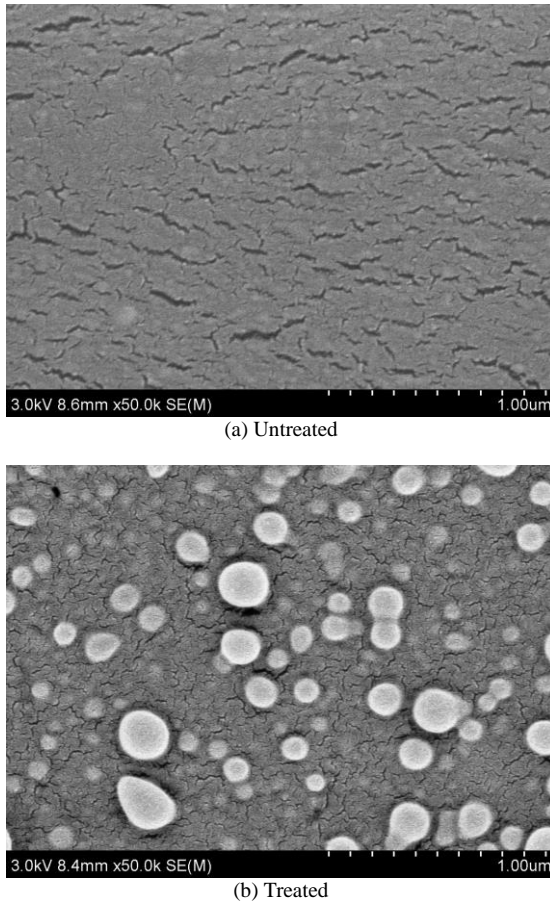


Fig. 7. SEM photographs of the surface of the PTFE films.

ACKNOWLEDGMENT

The authors would like to thank Mr. K. Suzuki (graduate student at Osaka Prefecture University), Dr. T. Onji, and Dr. T. Nishimura of Osaka Research Institute of Industrial Science and Technology for the experiments and analysis, supporting the research. This work was partly supported by JSPS KAKENHI Grant number 15K3932.

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