Preparation of PTFE Film with Adhesive Surface Treated by Atmospheric-Pressure Nonthermal Plasma Graft Polymerization

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Abstract—A surface modification technique for improving the adhesion of fluorocarbon polymer films such as PTFE (polytetrafluoroethylene), PFA (perfluoroalkoxy fluoroplastics) and PCTFE (polychlorotrifluoroethylene) is developed by using atmospheric-pressure argon and acrylic acid vapor nonthermal plasma. The results of the T-type peeling test show that the peeling strength of the treated PTFE film is approximately over 100 times greater than that of the untreated film. It is confirmed from XPS (X-ray photoelectron spectroscopy) and SEM (Scanning electron microscope) analyses that no chemical connections with F atoms exist on the surface and a hydrophilic layer is formed due to the plasma graft polymerization process. Using the present surface treatment apparatus, it is possible to bond A4 sized PTFE and metals without losing excellent physical properties of PTFE itself.

Index Terms—Nonthermal plasma, plasmas, thin films, fluorocarbon polymer, PTFE (polytetrafluoroethylene), adhesion improvement, graft-polymerization

I. INTRODUCTION

FLEXIBLE thin solid films made of fluorocarbon polymers such as PTFE (polytetrafluoroethylene, –[CF₂–CF₂]ₙ–), PFA (perfluoroalkoxy fluoroplastics, –[CF₂–CF₃]ₙ–[CF₂–CF(CF₃)]ₙ–), and PCTFE (polychlorotrifluoroethylene, –[CF₂–CFCl]ₙ–) have excellent properties in terms of flexibility, gas and moisture barriers, heat and fire resistances, chemical resistance, electric insulation, etc. Therefore, the applications of these films have been extended to various fields. However, because the molecular structure of fluorocarbon polymers is very stable and the polymers are inactive, it is difficult to adhere the polymers to other substances and to laminate them. If their adhesive property can be improved, applications in electrical devices such as multilayer flexible electric circuits and flexible organic EL (electro luminescence) displays with a long life are possible because of their higher gas and moisture barrier properties [1, 2].

In order to improve the adhesive properties of such films, liquid-phase etching is often used with the sodium-ammonia solution submerging method [3]. In this method, there are some problems as follows: the processing environment is poor, and a large amount of effluent is drained, which results in a significant environmental load. Further, the surface of the film is chemically damaged by the etching. As a result, not only the excellent optical penetration properties but the strength of the film are lost considerably.

In the present study, an innovative plasma surface treatment method is proposed for fluorocarbon polymer films such as PTFE. Although low-temperature NTP (nonthermal plasma) technologies improving the surface properties of fibers and polymers have been used for enhancing their adhesion [4, 5] and hydrophilicity [6], deepening the coloration [7], and shrink-proofing of woolen fabrics [8], the effectiveness is not so significant and does not last for longer time with NTP treatments only. In order to realize the effective and permanent surface treatment, the NTP treatment must be combined with another one such as chemical painting process [9, 10]. Based on a similar concept of the combined process, we have developed a new and effective NTP combined surface modification technique for polymer textiles using an atmospheric-pressure NTP method, followed by graft-polymerization [11, 12] of the hydrophilic monomer. This process is expressed as

\[ \text{NTP application: } R - F \rightarrow R\cdot + F\cdot \]  

Graft-polymerization:

\[ R\cdot + n(CH_2=CHCOOH) \rightarrow R - [C_2H_3COOH]_n^- \]  

where R is the main chains of C, H, O and F atoms in fluorocarbon polymer, and R• and F• are the radicals.

As compared with the ordinary chemical surface treatment for the films, such as the sodium-in-liquid-ammonia submerging method, this is a dry technique and generates a small environmental load. It is confirmed from XPS (X-ray photoelectron spectroscopy) and FTIR (Fourier transform infrared spectrophotometer) analyses that a transparent hydrophilic layer with a thickness of the order of 1 µm is formed on the film surface. The results of the T-type peeling test show that the peeling strength of the film is considerably
greater than that of the untreated film. The SEM (Scanning electron microscope) image of the film reveals a very smooth and flat surface.

II. EXPERIMENTAL APPARATUS AND METHODS

A. NTP Treatment Apparatus and Method

Figure 1 shows the experimental apparatus for the treatment of the A4 sized fluorocarbon polymers films. Industry Argon (purity = 99.99%) is used as the test gas. The fluorocarbon film (for example, thickness = 100 mm and size = 21 × 30 cm, maximum thickness of the sample is 20 mm) is placed on the conveyer belt and moved in the longitudinal direction. The NTP jets induced by an atmospheric-pressure Ar corona discharge are applied to the surface. The plasma torch is moved in the transverse direction. The entire A4 region can be treated with this apparatus.

The details of the electric circuit for the plasma jet system are shown in Fig. 2. This system (Plasma Stream PSC1002, Pearl Kogyo Co., Ltd.) comprises a single plasma torches driven by a 20 kHz pulse modulated AC power supply (pulse duty ratio = 99%, output voltage = 24 kV, pulse modulation frequency = 60 Hz, average input power = 500 W). The distance between the surface of the sample film and the heads of the plasma torch nozzle is fixed at 9 mm. A stainless container of 100 mL filled with the acrylic acid monomer liquid is heated with a ribbon heater. The temperature of the monomer is maintained constant at 40 ~ 70°C. Initially, the treatment chamber (volume is approximately 0.5 m³) is purged with the Ar of 15 L/min at atmospheric-pressure without plasma in order to remove the residual oxygen, which has negative influence on the graft-polymerization process. After the duration of purging for 5 min, the plasma jet is applied to the film surface with the Ar flow rate of typically 30 L/min and bubbling gas flow rate of typically 3 L/min. After the plasma torch nozzle goes forth and back in the transverse direction, it moves 1 cm in the longitudinal direction. The whole A4 sized region is treated continuously.

After treating the film, four kinds of evaluations of contact angle measurement, T-type peeling test, XPS and FTIR analyses, and SEM observation are carried out.

B. Evaluation Apparatus and Methods

The PTFE film treated by the plasma graft-polymerization apparatus are tested for hydrophilicity, adhesive properties, molecular analysis, chemical structure, and surface morphology.

The hydrophilicity is determined from the contact angle of a pure water droplet. In the present study, the contact angle of a 5
µL droplet at the film surface is measured using goniometry (CA-VE, Kyowa Kaimen Kagaku Co.). In the T-type peeling test based on the JIS (Japanese Industrial Standard) No. K 6854, after the epoxy resin (E-set, Konishi Co., Ltd.) is coated on half the surface of the tested PTFE samples (total length = 100 mm, coated length = 50 mm, width = 25 mm) with a thickness of 250 µm using an applicator, the samples are glued to an aluminum plate. After the samples are dried for 24 hours at a constant temperature (25°C) with a load of 5 N applied to harden the epoxy resin. The time-dependent peeling strength and maximum peeling strength values are measured using a measurement system (AG-10kNG, Shimadzu Co., Ltd.). The peeling speed of the aluminum plate is maintained constant at 100 mm/min.

Information regarding the chemical bonding and elemental composition of the untreated film and the treated films is obtained by XPS measurements using a spectrometer (Kratos ESCA-3300) and employing a Mg Kα (1253.6 eV) X-ray source. The spectral measurements are performed at a voltage of 8 kV, current of 30 mA, and pass energy of 32 eV with an energy step of 0.1 eV. The morphologies of the graft-polymerization surfaces are observed with a SEM (model ESEM-2700, Nikon Co. Ltd.; magnification: 2000 ～ 5000, acceleration voltage: 15 kV).

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Contact Angle

Figure 3 shows the measured contact angles for a pure water droplet on the film surface untreated and treated by three kinds of monomers of acrylic acid (CH₂=CHCOOH), hydroxyethyl methacrylate (H₂C=C(CH₃)COOCH₂CH₂OH) and glycidyl methacrylate (C₇H₁₀O₃) in one second after the droplet reaches the surface. In this table, the smaller contact angles indicate a higher hydrophilicity of the surface. The contact angles of the untreated PTFE film are relatively large, 104°, respectively. However, after these processes, high hydrophilicities or lower contact angles are obtained for the PTFE film. In particular, process with acrylic acid monomer results in the smallest contact angle of 26°. It is observed that the contact angle decreased gradually and saturated approximately 10° in 6 hours.

B. Peeling strength

Figure 4 shows the results of the T-type peeling strength tests. In this figure, the horizontal axis means the temperature of acrylic acid monomer and the vertical axis means the peeling strength of 25 mm width PTFE film. As compared to the untreated samples (peeling strength is 0.5 N), the treated samples exhibit better adhesive strengths. For the film treated by NTP only without monomer gas injection, the peeling strength of 6.7 N is achieved. The peeling strength increases with increase in the temperature and the highest peeling strength of 35.8 N is achieved at the temperature of 60°C. This value is approximately seventy times larger than that for the untreated one. At the temperature more than 60°C, the peeling strength becomes lower because the monomer may be changed to liquid inside the injection tube and the gas concentration may decreases with the present apparatus.

C. XPS analysis

Figure 5 shows the XPS spectra of C1s peaks for the untreated PTFE sample. In this figure, the peak for –CF₂⁻ (a difluoromethylene group), which is the origin of the hydrophobicity, is detected at 294.5 eV from the decomposition of the total C1s spectrum.

Fig. 5 XPS spectra of C1s peaks for untreated PTFE sample

Figure 6 shows the XPS spectrum of C1s peaks for the PTFE sample treated by process A. The peaks for –COO⁻ (carboxyl group), –C=O (carbonyl group), –C–O⁻ and –C–C–, –CH₂– are detected approximately at 289 eV, 287.5 eV, 286 eV, and 285 eV, respectively, from the decomposition of the C1s total peak. In general, when functional groups such as –C–O⁻, –C=O, and –COO⁻ are incorporated into a polymer surface, the surface becomes hydrophilic and the surface adhesion is improved. Furthermore, because –CF₂⁻ structure are not detected at the surface, it is known that the surface is covered with the plasma graft-polymerization layer of acrylic acid.

Table 1 shows the results of the elementary analysis or the ratio of C, O, F and N atoms on the film surfaces. The PTFE
films are treated with three kinds of treatment: (a) sodium-in-ammonia treatment (not plasma treatment) (b) plasma graft polymerization with acrylic acid monomer and (c) plasma graft polymerization with formic acid monomer. As well as Fig. 4, the peaks for O$_{1s}$, F$_{1s}$ and N$_{1s}$ spectra are measured. The ratios of the C, O, F and N atoms on the surfaces are calculated as area ratios from the decompositions of C$_{1s}$, O$_{1s}$, F$_{1s}$ and N$_{1s}$ peak spectra.

The atomic ratios of the untreated PTFE film are C: O: F = 27.8: 0.1: 72.1. A relatively large amount of F atoms leads to hydrophobic property. At the surface of the sample treated by the process (b), the atomic composition of F considerably decreases down to 11.5%, although those of C and O increase up to 30.4% and 58.1%, respectively, as well as the treatment (a). It is confirmed that few F atoms and the hydrophilic layer consisted of hydrophilic functional groups such as –COO– (carboxyl group), –C=O (carbonyl group) exist on the surface due to the graft-polymerization process. At the present, plasma graft polymerization with formic acid monomer is less effective at the present.

D. FTIR Analysis

Figures 7 (a), (b) shows the FTIR spectra for the untreated PTFE and the PTFE treated by the plasma graft polymerization with acrylic acid. In treated 1 sample, the plasma torch nozzle goes forth and back once in the transverse direction. In treated 2 sample, the plasma torch nozzle goes forth and back ten-times in the transverse direction. Therefore, stronger peaks are observed in treated 2 sample.

In the case of the treated samples, the peak for –COOH– is observed at a wave number of approximately 1700 cm$^{-1}$, which
does not appear in the case of the untreated sample. It is inferred from this result that the –COOH– base is present at the surface of the films and that it improves the hydrophilicity and adhesive property of the surface. Further, the small peak for –CH2– is observed at wave numbers of approximately 2850 and 2925 cm\(^{-1}\), but does not appear in the case of the untreated sample. Further, in all samples, the peaks for –CF2– and –CF3 are detected at approximately 1100 ~ 1200 cm\(^{-1}\), but are not detected by XPS in the surface analysis of the treated samples. Because the FTIR can analyze deeper chemical structure than XPS, it is concluded that the graft-polymerization layer is extremely thin and that the inner chemical structure slightly changes.

E. SEM Observations

Figures 8(a)–(c) show the surfaces of the PTFE films as observed using the SEM. Figure 8(a) shows the surface of the untreated PTFE film. Some granular unevenness is observed because the film is originally prepared from PTFE powder. Figure 8(b) shows the surface of the PTFE film treated by the plasma graft polymerization. In this photograph, the unevenness disappears due to the grafted polymer on the surface and the surface is almost flat. Figure 8(c) shows the surface of the PTFE film treated by a traditional treatment technology, sodium-in-liquid-ammonia method [2]. There are some drawbacks in this method: the processing environment is poor and a large amount of effluent is drained, which results in significant environmental load. Although the adhesion property is significantly improved, the surface morphology is considerably changed and chemically damaged by the etching, as is observed in Fig. 8(c). Further, because the surface becomes brown and the excellent optical penetration property is totally lost, it is difficult to apply this film to electrical flexible display devices such as electric papers. In view of these observations, we believe that the present plasma jet treatment has several advantages.

Figure 9 shows nickel electroless metal plating on the PTFE treated by the present plasma graft polymerization. High adhesive metal plating can be realized first for the PTFE flexible film, which was very difficult with ordinary surface treatment. The detailed procedure has been already reported by the authors [13].

![Fig. 8 SEM photographs of PTFE film surfaces](image)

![Fig. 9 Nickel electroless metal plating on the PTFE (treated by A4 apparatus)](image)
IV. CONCLUSIONS

An innovative and environmentally safe technology for the surface modification for fluorocarbon polymers is developed using an atmospheric-pressure NTP application followed by the graft-polymerization of the hydrophilic monomer. The main results are as follows:

(1) After the plasma graft-polymerization process, high hydrophilic properties or small contact angles are obtained for fluorocarbon polymer A4 sized films. The highest hydrophilicity or the smallest contact angle of 26° with acrylic acid monomer.

(2) In the T-type peeling strength tests, the samples treated by the plasma graft-polymerization processes show more excellent adhesive properties compared to the untreated samples. The highest T-type peeling strength of 35.8 N per 25 mm width is obtained. This value is approximately seventy times greater than that for the untreated film (0.5 N).

(3) From the results of the XPS surface analysis for the treated PTFE film, the peaks for –COO–, –C=O–, –C–O– and –C–C–, –C–H– are detected from the decomposition of the C1s total peak. As a result of the elemental analysis of the XPS spectra, the atomic ratios of the PTFE film treated by the present apparatus with acrylic acid are C: O = 58.1: 30.4: 11.5. It is confirmed that few F atoms and hydrophilic layer consisted of hydrophilic functional groups exist on the surface due to the grafting process.

(4) In the FTIR analysis of the treated samples, the peak for –COOH– is observed at a wave number of approximately 1700 cm⁻¹, which does not appear in the case of the untreated sample. It is inferred from this result that the –COOH– base is present at the surface of the films and improves the hydrophilicity and adhesive properties of the surface.

(5) The SEM image of the treated film reveals the smooth and flat surface. It is confirmed that a transparent, hydrophilic, adhesive, and uniform permanent layer with a thickness of an order of 0.1 µm, is formed on the film surface.

(6) High adhesive metal plating can be realized first for the PTFE flexible film, which was very difficult with ordinary surface treatment.

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