

IEEE Copyright Notice

© 2022 IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.

Date of publication: October 10, 2022

DOI: 10.1109/TIA.2022.3213019

Cite as:

T. Kuroki, M. Narita, T. Kageyama, H. Yamasaki, T. Matsumoto, T. Ida, and M. Okubo, Higher Adhesion Strength over 10 N/mm between Rubber and Fluoropolymer Film When Treated by Atmospheric Plasma-Graft Polymerization, *IEEE Transactions on Industry Applications*, 59, 1, pp. 450-455, October 2022.

Higher Adhesion Strength over 10 N/mm between Rubber and Fluoropolymer Film when Treated by Atmospheric Plasma-Graft Polymerization

Tomoyuki Kuroki, *Member, IEEE*, Mitsuru Narita, Takumi Kageyama, Haruhiko Yamasaki, *Member, IEEE*, Takuya Matsumoto, Tsuyoshi Ida, and Masaaki Okubo, *Senior Member, IEEE*

Abstract—An evaluation of the adhesion between rubber and fluoropolymer films treated by atmospheric plasma-graft polymerization is conducted to realize a low-permeation fuel rubber hose covered with fluoropolymer. The low-permeation fuel rubber hose is important for reducing vehicular evaporative emissions. Although fluoropolymers have extremely low permeability for fuel, it is difficult to bond them with other materials, such as rubber, because of their low adhesive properties. Plasma surface modification has been investigated to improve the adhesive properties of fluoropolymers. However, it is difficult to realize effective and permanent surface treatment using plasma alone. Based on the new and effective combined plasma surface-modification technique for fluoropolymer films, we previously proposed an atmospheric-pressure plasma method followed by graft polymerization of hydrophilic monomers such as acrylic acid ($\text{CH}_2=\text{CHCOOH}$). In this study, three types of rubber, isobutylene isoprene rubber (IIR), ethylene acrylic elastomer (AEM), as well as white-colored ethylene acrylic elastomer (white AEM), and two types of fluoropolymer films, denatured PFA-1 and denatured PFA-2, were prepared. The treated fluoropolymer film and rubber were adhered using vulcanized adhesion, and then the 180° peeling strength test was conducted. The results show that an average peeling strength of 12.6 N/mm and a maximum peeling strength of 15.3 N/mm, which are over 10 N/mm, are attained for the sample of vulcanized bonding of the treated denatured PFA-1 and AEM.

Index Terms—Adhesion, atmospheric-pressure plasmas, graft-polymerization, surface treatment, fluoropolymer

I. INTRODUCTION

VEHICULAR evaporative emissions are caused by leaks and the permeation of fuel from fuel tanks and piping [1]. Although vehicular evaporative emissions have been neglected outside the United States, they are recognized as an important source of volatile organic compounds (VOCs) with growing concern with respect to

environmental problems [2]. To reduce leaks and permeation of fuel from a fuel rubber hose, a multilayered hose comprising a rubber hose and fluoropolymer film, as shown in Fig. 1, was investigated.

Fluoropolymers have excellent properties in terms of their flexibility, gas and moisture impermeability, heat and fire resistance, chemical resistance, and electrical insulation. Therefore, these films have been applied in numerous fields [3]. However, because the molecular structure of fluoropolymers is very stable and the polymers therefore being unreactive, it is difficult to bond these polymers with other substances. Therefore, the introduction of functional groups that contribute to the adhesion properties of fluoropolymers as constituent materials or by surface modification is necessary. Liquid-phase etching is a conventional method for improving the adhesive properties of such films. However, the processing environment is poor and a large amount of effluent is drained, resulting in a significant environmental load. Furthermore, the surface of the film was chemically damaged by etching. This considerably reduces the excellent visible light transmission properties and strength.

As an alternative method, plasma surface modification has been investigated [4]–[10]. Although plasma technologies that improve the surface properties of fibers and polymers have been used to enhance adhesion [4, 5] and hydrophilicity [6, 7], deeply dye silk fabrics [8], and make shrink-proof wooden fabrics [9], the effects on fluoropolymer films have not been shown to be either significant or long-lasting [11]. To improve atmospheric plasma surface treatment, combinations of various gases such as O_2 , He, Ar, NH_3 , N_2 , H_2 , B_2H_6 , and H_2O have been employed [12, 13]. Furthermore, heat-assisted plasma treatment has been shown to improve the strength and durability of polytetrafluoroethylene (PTFE) adhesion [14].

We previously proposed an atmospheric-pressure plasma

Manuscript received 20 January 2022; revised 21 July 2022; accepted 21 September 2022. Date of publication ; date of current version . Paper 2022-EPC-0080, presented at the 2021 IEEE Industry Applications Society Annual Meeting, BC, Canada, Oct. 10–14, 2021, and approved for publication in the IEEE TRANSACTIONS ON INDUSTRY APPLICATIONS by the Electrostatic Processes Committee of the IEEE Industry Applications Society (*Corresponding author: Tomoyuki Kuroki*).

Tomoyuki Kuroki, Haruhiko Yamasaki, and Masaaki Okubo are with the Department of Mechanical Engineering, Osaka Prefecture University and Osaka Metropolitan University, Sakai 599-8531, Japan (e-mail: kuroki@omu.ac.jp; hyamasaki@omu.ac.jp; mokubo@omu.ac.jp).

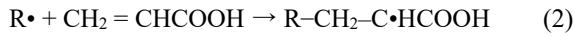
Mitsuru Narita and Takumi Kageyama are with the Department of Mechanical Engineering Osaka Prefecture University, Sakai 599-8531, Japan (e-mail: szb03104@gmail.com; kagetakumi@icloud.com). Research

Takuya Matsumoto and Tsuyoshi Ida are with the Department of & Development, Togawa Rubber Co., LTD, Sakai 599-8244, Japan (e-mail: takuya-matsumoto@togawa.co.jp; tsuyoshi-ida@togawa.co.jp).

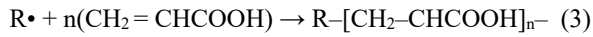
Color versions of one or more of the figures in this article are available online at <http://ieeexplore.ieee.org>

method followed by graft polymerization of hydrophilic monomers such as acrylic acid ($\text{CH}_2=\text{CHCOOH}$). The plasma-graft polymerization process using acrylic acid as a monomer is as follows:

1) *NTP application*



2) *Graft polymerization*



where R represents the main chain containing other side chains 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 radicals. By plasma irradiation to fluoropolymers, the R-F bond is cleaved, and $\text{R}\cdot$ is generated as shown in reaction (1), followed by combining $\text{R}\cdot$ with acrylic acid as shown in reactions (2) and (3). Consequently, the uneven-sized spherical acrylic acid polymers with diameters less than 0.5 μm are formed on the surface of the treated fluoropolymer, whereas the surface of the untreated fluoropolymer appears to be smooth [15]. Thus, the surface morphology of treated fluoropolymer can contribute to improving the adhesive property.

In the study of adhesion between a PTFE film and butyl rubber for application to medical equipment [16], we attained an extremely strong reinforced adhesion between a PTFE film and butyl rubber using atmospheric pressure plasma graft polymerization. The highest obtained 180° peeling strength was 3.88 N per 1 mm width. However, a higher peeling strength of more than 10 N/mm is required for application to a low-permeation fuel rubber hose. Attaining this value is difficult when done by improving only the constituents of the fluoropolymer material. In this study, we evaluated the adhesion between rubber and denatured PFA film, which is a copolymer of tetrafluoroethylene and perfluoroalkyl vinyl ether in which the main chain of the third monomer was added, and the film was treated by atmospheric plasma-graft polymerization to realize a low-permeation fuel rubber hose covered with fluoropolymer film [17].

II. EXPERIMENTAL EQUIPMENT AND METHODS

A. Fluoropolymer and Rubber

The two types of denatured PFA films, which are copolymers of tetrafluoroethylene and perfluoroalkyl vinyl ether, in which the main chain of the third monomer was added, were prepared as fluorocarbon polymer films. We refer to these denatured PFA-1 and denatured PFA-2. Denatured PFA-1 has a reactive group and can adhere directly to rubber, such as nitrile-butadiene rubber (NBR) and epichlorohydrin rubber (ECO), by cross-linking during vulcanization, but has less mechanical properties than PFA. Denatured PFA-2 has a lower adhesive property than that of denatured PFA-1 but has excellent low permeability to volatile chemicals, water vapor, and gases; furthermore, it has almost the same mechanical properties as PFA. Three types of rubber (isobutylene isoprene rubber (IIR),

ethylene acrylic elastomer (AEM), and white-colored ethylene acrylic elastomer (white AEM), which contain silicon dioxide (SiO_2) instead of carbon black as filler, were used. **Table I** lists the specifications of IIR, AEM, and white AEM. AEM and white AEM have a stronger tensile strength than IIR.

B. Plasma-Graft Polymerization Treatment

Fig. 2 shows the experimental setup for the NTP graft polymerization process used to treat the A4-sized fluoropolymer films. Industrial argon (purity = 99.99%) was used as the plasma gas. A grounded copper-laminated glass epoxy plate, which was covered with a 0.2 mm thick PTFE film, was used as the sample holder and placed on a conveyor belt that moved along the longitudinal direction. The sample of the fluoropolymer film (length = 150 mm, width = 150 mm, and thickness = 1 mm) was placed on the sample holder. NTP jets induced by gliding arc discharge at atmospheric pressure are emitted from a plasma nozzle with an appropriate cover [18], and they are applied to the sample surface of the fluoropolymer film. The entire sample was treated using this equipment. The power supply system (PSC 1001, Pearl Kogyo Company, Ltd.) comprises of 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 gliding arc discharge was generated by applying 180 degree phase shift voltages between two discharge electrodes. The waveforms of applied voltages to the two discharge electrodes, current, and instantaneous discharge power are shown in **Fig. 3**. The maximum of difference between two applied voltages is 2.48 kV and the discharge power is calculated as 48.3 W. The distance between the sample surface of the fluoropolymer film and the head of the plasma jet nozzle was fixed at 9 mm for the film during the experiment.

A pair of evaporation containers (L 296 mm \times W 19 mm \times D 59 mm) filled with 100 g of acrylic acid monomer liquid (purity = 98 mass%, FUJIFILM Wako Pure Chemical Corporation) was used to generate acrylic acid monomer vapor. It was heated using a heater located under the container. The two containers were placed on either sides of the conveyor belt to achieve a uniform monomer concentration. The temperature of the monomer was maintained at 55°C using a thermal controller. Because of the negative influence of oxygen on the graft polymerization process, the treatment chamber (with an approximate volume of 0.5 m^3) was purged with Ar at atmospheric-pressure for 30 min prior to NTP treatment until the treatment was finished. In addition, the gaps between the left and right sides of the treatment chamber and the conveyor belt were covered with brushes and Ar gas curtains to prevent the inflow of air. The total flow rate of the purge and gas curtain was 20 L/min. After 30 min of purging, the plasma jet was applied to the film surface at an Ar flow rate of 40 L/min. The increase in gas temperature is suppressed by Ar flow, and a low temperature (typically 80°C) is realized. Although slight damage may be caused on the fluoropolymer surface by NTP treatment, the properties of fluoropolymer are not impaired. The plasma jet nozzle moved in the transverse direction at a

velocity of 4 mm/s until it reached the edge of the film, and then it moved 1 cm in the longitudinal direction.

C. Vulcanized Rubber-Fluoropolymer Bonding

The treated fluoropolymer and unvulcanized rubber were placed into a rectangular hole (50 mm × 100 mm) of a metal mold (150 mm × 150 mm × 5 mm). To create a gripping margin, a polyethylene terephthalate (PET) film (50 mm × 25 mm × 0.25 mm) was placed between the treated fluoropolymer and unvulcanized rubber. Subsequently, vulcanized rubber-fluoropolymer bonding was conducted at a pressure of 1 MPa and a temperature of 150°C for 60 min using a hot press machine, as shown in Fig. 4. The polymers of acrylic acid formed on the treated fluoropolymer hereby reacts with cross-linking material contained in unvulcanized rubber, resulting in reinforced bonding between fluoropolymer and rubber [16]. The accomplished sample was cut into fifths, and the middle three pieces were used as a sample for the peeling test. Meanwhile, the untreated fluoropolymer was not bonded to the rubber.

D. Peeling Test

The 180° peeling test, which follows Japanese Industrial Standards K6256-1, is performed to evaluate the peeling strength between the treated fluoropolymer and rubber using universal testing systems (model 33R4444, Instron). The samples were 100 mm in length, 10 mm in width, and 6 mm in thickness. The rubber and fluoropolymer films were fixed by the upper and lower grips, respectively. The peel speed was 50 mm/s. Fig. 5 shows photographs of a peeling test sample before and during the test. When the bonding between the rubber and the fluoropolymer film is extremely strong, the peeling strength cannot be properly measured because of the extension of the rubber. Therefore, the stretched rubber is cut in by a box cutter as needed.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Fig. 6 shows the results of the peeling tests for the sample of vulcanized bonding between the treated denatured PFA-1 and rubber. The thick line represents the average value of three trials, and the two thin lines denote the standard deviations. The average peeling strength at a stroke of 50–100 mm is calculated. Fig. 6(a) shows the results of the IIR. The results show that the average peeling strength is 6.46 N/mm. Furthermore, the variability in the data seems to be small. Fig. 6(b) shows the results of AEM. Although the variability of data is larger than that of IIR, the average peeling strength of 12.6 N/mm, which fully meets the requirements for being applied to a fuel hose, is attained. Fig. 6(c) shows the results of the white AEM. The average peeling strength is 6.15 N/mm that is slightly lower than that of IIR. However, the variability of the data is the smallest among the three kinds of rubber.

Fig. 7 shows the results of the peeling tests for the sample of vulcanized bonding between the treated denatured PFA-2 and rubber. Fig. 7(a) shows the result of IIR. The average peeling strength is 5.46 N/mm that is lower and the variability of data seems to be almost the same as that of denatured PFA-1. Fig.

7(b) shows the result of AEM. Although the variability of data is larger than that of IIR, the average peeling strength of 9.76 N/mm was the highest, and the variability of data was larger among the three types of rubber. This is the same tendency as that for denatured PFA-1. Fig. 7(c) shows the results of the white AEM. The average peeling strength is 5.33 N/mm which is slightly lower, whereas the variability of data is larger than that of IIR.

Table II lists the maximum peeling strengths and failure modes for each sample. The symbols R and D denote adherent failure and adhesive failure, respectively. Substrate failure, namely breakage of denatured PFA, did not occur. The maximum peeling strength of the denatured PFA-1 samples was higher than that of the denatured PFA-2. Although the third monomer contained in the denatured PFA and constituent ratios of denatured PFA-1 and denatured PFA-2 are not disclosed, it is considered that the third monomer is presumably chlorotrifluoroethylene [19]. The ratio of chlorotrifluoroethylene in denatured PFA seems to affect its peeling strength. Furthermore, the failure mode of the samples of vulcanized bonding between the treated denatured PFA-1 and IIR was adherent failure. The maximum peeling strength does not attain 10 N/mm; however, the sufficient peeling strength is realized because the tensile strength of IIR is 9.2 MPa from Table I. For the samples of vulcanized bonding between the treated denatured PFA-1 and AEM, the maximum peeling strength of them is even higher than that of the samples of vulcanized bonding between the treated denatured PFA-1 and IIR. In addition, the failure mode of the three samples was mostly adherent failure, resulting in strong bonding. However, the maximum peeling strength of the samples of vulcanized bonding between the treated denatured PFA-1 and white AEM was lower than that of the samples of vulcanized bonding between the treated denatured PFA-1 and AEM. The failure mode of the three samples was also only or mostly adhesive failure. The failure modes of the samples of vulcanized bonding between the treated denatured PFA-2 and IIR or AEM were both adherent failure and adhesive failure because the maximum peeling strength of the denatured PFA-2 samples is lower. However, the failure mode of the samples of vulcanized bonding between the treated denatured PFA-2 and white AEM is the same as that of the treated denatured PFA-1 and white AEM, regardless of the type of fluoropolymer. This indicates that interfacial peeling mainly occurs between the graft polymer layer and white AEM. Therefore, the vulcanized bonding condition and monomer need to be optimized to increase the peeling strength of the white AEM sample.

IV. CONCLUSION

The evaluation of adhesion between rubber and denatured PFA film treated by atmospheric plasma-graft polymerization was conducted with 180° peeling tests to realize a low-permeation fuel rubber hose. For the samples of rubber and denatured PFA-1, the average and maximum peeling strength obtained are 6.46 and 9.2 N/mm for IIR, 12.6 and 15.3 N/mm for AEM, 6.15 and 7.3 N/mm for white AEM. For the samples of rubber and

R2022-EPC-0080.R1

denatured PFA-2, the average and maximum peeling strength of 5.46 and 7.8 N/mm for IIR, 9.76 and 13.0 N/mm for AEM, 5.33 and 7.5 N/mm for white AEM are obtained. The results showed that the effect of surface modification using plasma-graft polymerization on denatured PFA-1 was higher than that of denatured PFA-2. This study demonstrated the effectiveness of this method in improving the adhesion of rubber and denatured PFA.

ACKNOWLEDGMENT

The authors thank Mr. M. Murata, a student at Osaka Prefecture University, for carrying out the experiments.

REFERENCES

- [1] H. Yamada, "Contribution of evaluative emissions from gasoline vehicles toward total VOC emissions in Japan," *Sci. Total Environ.*, vol. 449, pp.143–149, 2013.
- [2] H. Liu, H. Man, M. Tschantz, Y. Wu, K. He, and J. Hao, "VOC from vehicular evaporation emissions: status and control strategy," *Environ. Sci. Technol.*, vol. 49, pp.14424–14431, 2015.
- [3] H. Teng, "Overview of the development of the fluoropolymer industry," *Appl. Sci.*, vol. 2, no. 2, pp. 496–512, 2012.
- [4] N. Inagaki and H. Yasuda, "Adhesion of glow discharge polymers to metals and polymers," *J. Appl. Polym. Sci.*, vol. 26, no. 10, pp. 3333–3341, Oct. 1981.
- [5] A. Sarani, N. D. Geyter, A. Y. Nikiforov, R. Morent, C. Leys, J. Hubert, and F. Reniers, "Surface modification of PTFE using an atmospheric pressure plasma jet in argon and argon + CO₂," *Surf. Coat. Technol.*, vol. 206, pp. 2226–2232, 2012.
- [6] A. M. Wrobel, M. Kryszewski, W. Rakowski, M. Okoniewski, and Z. Kubacki, "Effect of plasma treatment on surface structure and properties of polyester fabric," *Polymer*, vol. 19, no. 8, pp. 908–912, Aug. 1978.
- [7] H. S. Salapare III, F. Guittard, X. Noblin, E. T. Givenchy, F. Celestini, and H. J. Ramos, "Stability of the hydrophilic and superhydrophobic properties of oxygen plasma-treated poly(tetrafluoroethylene) surfaces," *J. Colloid and Interface Sci.*, vol. 396, pp. 287–292, 2013.
- [8] Y. Iriyama, T. Mochizuki, M. Watanabe, and M. Utada, "Plasma treatment of silk fabrics for better dyeability," *J. Photopolymer Sci. Technol.*, vol. 15, no. 2, pp. 299–306, 2002.
- [9] J. R. Roth, *Industrial Plasma Engineering, Application to Nonthermal Plasma Processing*. Bristol, U.K.: Inst. Phys. Publishing, 2001, pp.383–395.
- [10] C. Borcia, G. Borcia, and N. Dumitrascu, "Atmospheric-pressure dielectric barrier discharge for surface processing of polymer films and fibers," *IEEE Trans. Plasma Sci.*, vol. 37, no. 6, pp. 941–945, Jun. 2009.
- [11] U. Lappan, H. M. Buchhammer, and K. Lunkwitz, "Surface modification of poly(tetrafluoroethylene) by plasma pretreatment and adsorption of polyelectrolytes," *Polymer*, vol. 40, no. 14, pp. 4087–4091, 1999.
- [12] K. Furuse, Y. Sawada, K. Takahashi, M. Kogoma, and K. Tanaka, "Defluorination Treatment of Polytetrafluoroethylene by B₂H₆/He Plasma at Atmospheric Pressure," *J. Photopolymer Sci. Technol.*, vol. 28, no. 3, pp. 465–469, 2015.
- [13] M. Kogoma, K. Takahashi, and K. Tanaka, "Surface treatment of fluorinated polymers using atmospheric pressure glow discharge system," *J. Photopolymer Sci. Technol.*, vol. 29, no. 3, pp. 421–425, 2016.
- [14] Y. Ohkubo, M. Shibahara, K. Ishihara, A. Nagatani, K. Honda, K. Endo, and K. Yamamura, "Effect of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated polytetrafluoroethylene (PTFE)," *J. Adhesion*, vol. 95, no. 3, pp. 242–257, 2019.
- [15] T. Kuroki, M. Nakamura, K. Hori, and M. Okubo, "Effect of monomer concentration on adhesive strength of PTFE films treated with atmospheric-pressure nonthermal plasma graft polymerization," *J. Electrostat.*, 108, 103526, 2020.
- [16] M. Okubo, T. Onji, T. Kuroki, H. Nakano, E. Yao, and M. Tahara, "Molecular-level reinforced adhesion between rubber and PTFE film treated by atmospheric plasma polymerization," *Plasma Chem. Plasma Process*, 36, pp. 1431–1448, 2016.
- [17] T. Kuroki, M. Narita, T. Kageyama, H. Yamasaki, T. Matsumoto, T. Ida, and M. Okubo, "Higher Adhesion Strength over 10 N/mm between Rubber and Fluoropolymer Film Treated by Atmospheric Plasma-Graft Polymerization," in *Conf. rec. IEEE Ind. Appl. Soc. Annu. Meeting*, Vancouver, BC, Canada, 2021, pp.1–4.
- [18] K. Hori, S. Fujimoto, Y. Togashi, T. Kuroki, M. Okubo, "Improvement in molecular-level adhesive strength of PTFE film treated by atmospheric plasma combined processing," *IEEE Trans. Ind. Appl.*, 55, pp. 825–832, 2019.
- [19] Method for recovering fluorine-containing ether, by Y. Zenke, T. Isaka, R. Fukagawa, and T. Shimono. (2014.7.4). P5569660 (in Japanese) [Online]. Available: <https://www.j-platpat.inpit.go.jp/c1800/PU/JP-5569660/0CC5854AB4AFEEDA4304837B47A5518A1E7E86C69B90332C45FCC928A9A4AFB0/15/ja>.

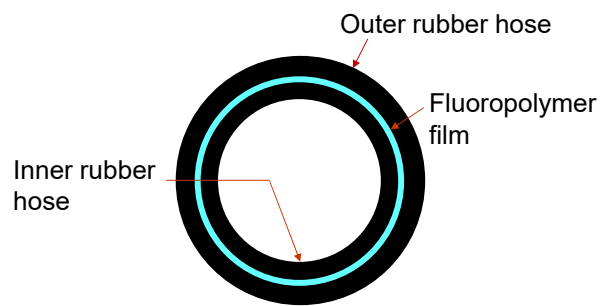


Fig. 1. Cross section of multilayer fuel hose.

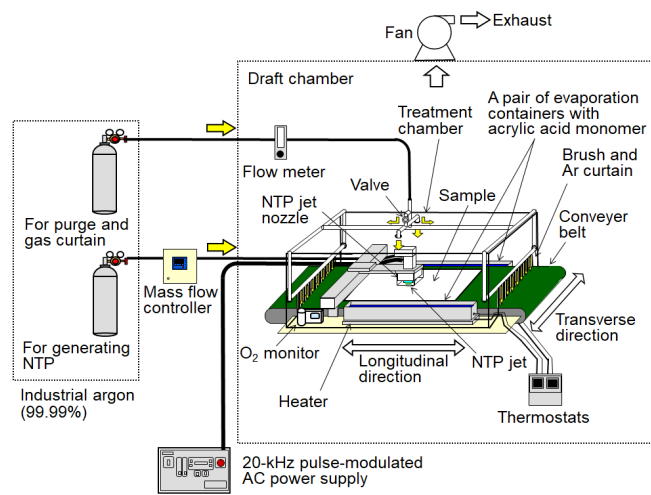


Fig. 2. Experimental setup for the NTP graft polymerization process used to treat A4-sized fluoropolymer films.

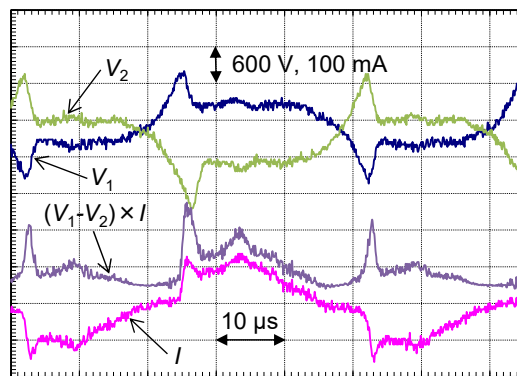


Fig. 3. The waveforms of applied voltages to the two discharge electrodes V_1 and V_2 , current I , and instantaneous discharge power $(V_1 - V_2) \times I$.

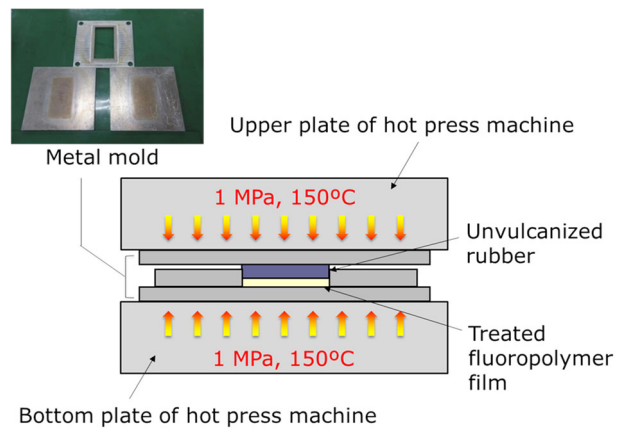


Fig. 4. Vulcanized rubber-fluoropolymer bonding using a hot press machine.

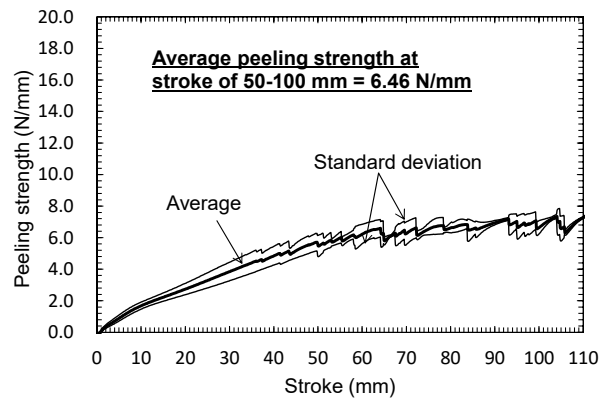


(a) before test

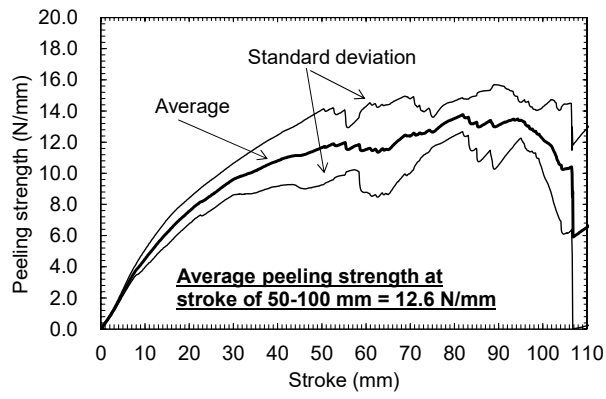


(b) under test

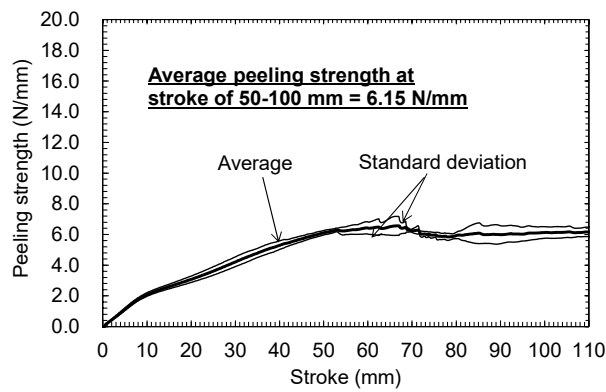
Fig. 5. Photographs of a peeling test sample before and under test.



(a) IIR

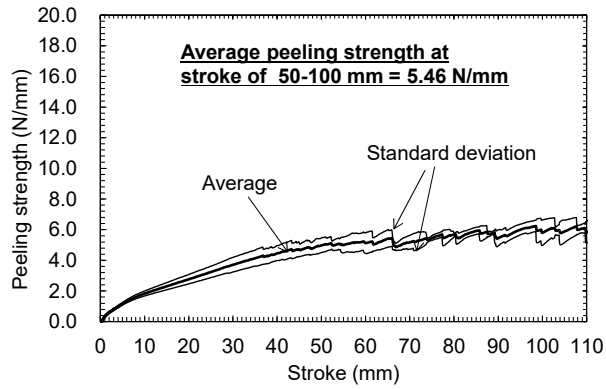


(b) AEM

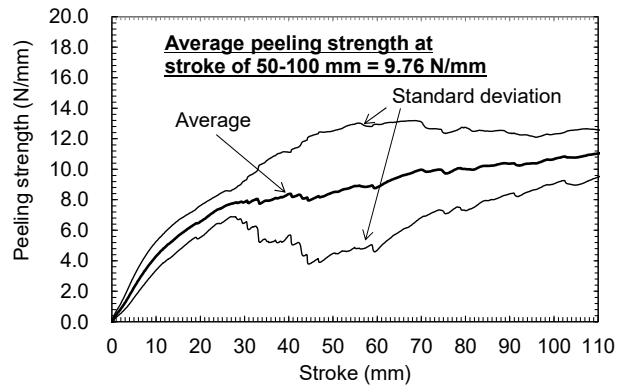


(c) white AEM

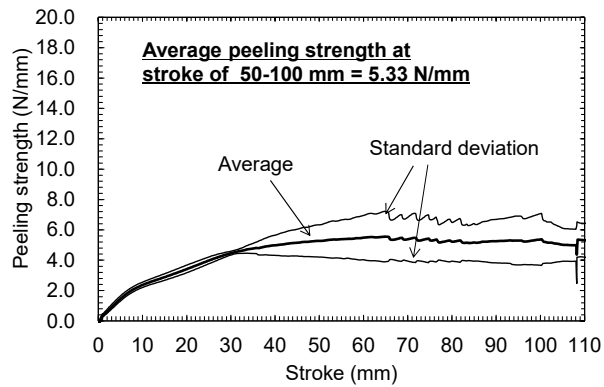
Fig. 6. Results of peeling tests for the sample of vulcanized bonding between the treated denatured PFA-1 and rubber.



(a) IIR



(b) AEM



(c) white AEM

Fig. 7. Results of peeling tests for the sample of vulcanized bonding between the treated denatured PFA-2 and rubber.

TABLE I SPECIFICATIONS OF IIR, AEM, AND WHITE AEM

Rubber type	Hardness (Type A durometer)	Tensile strength MPa	Elongation %
IIR	40	9.2	1000
AEM	59	13.4	580
white AEM	50	13.8	630

TABLE II THE MAXIMUM PEELING STRENGTHS AND FAILURE MODES FOR EACH SAMPLE.

Rubber type	Test No.	Denatured PFA-1		Denatured PFA-2	
		Maximum peeling strength N/mm	Failure mode	Maximum peeling strength N/mm	Failure mode
IIR	1	9.0	only R	6.7	R and D
	2	9.2	only R	6.9	R and D
	3	8.9	only R	7.8	R and D
AEM	1	15.3	mostly R and slightly D	13.0	mostly R and slightly D
	2	14.6	mostly R and slightly D	12.2	R and D
	3	14.3	mostly R and slightly D	11.5	R and D
white AEM	1	7.3	mostly D and slightly R	4.5	only D
	2	6.7	only D	4.9	only D
	3	6.4	only D	7.5	mostly D and slightly R