Enhanced Fluoropolymer Surface Adhesion by a Plasma Hybrid Process—Metal Plating Technology and Its Application to Millimeter-Wave Devices

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Abstract An improvement of the adhesiveness of PTFE/plastic using a plasma hybrid process, metal plating technology, and its application to millimeter-wave devices are described. Atmospheric-pressure plasma graft polymerization (also called "atmospheric-pressure plasma hybrid surface treatment"), which has been developed by the group of the author, is presented as an innovative surface treatment method to improve the PTFE adhesiveness and enable surface plating with minimal impact on the environment. First, the applicability of PTFE/plastics to millimeter-wave devices is briefly described, while next section presents the atmospheric-pressure plasma hybrid surface treatment that enables plating on PTFE. Next, methods to assess the effect of the surface treatment on PTFE metal plating are described. Final section describes several examples of improved strength of fiber-reinforced composite materials, which have a low dielectric constant similar to that of PTFE and can be used in radar domes. Some trial production results using this plasma hybrid surface treatment technology are also provided. Long-term durable adhesion properties of the surface are improved by this type of plasma treatments.

1 Introduction

Fluoropolymer plastic materials, such as polytetrafluoroethylene (PTFE, $-(CF_2-CF_2)_n-$), perfluoroalkoxy fluoroplastics (PFA, $-(CF_2-CF_2)_n-[CF_2-CF(OCF_2CF_2CF_3)]_m-$), and polychlorotrifluoroethylene (PCTFE, $-(CF_2-CFCl)_n-$), exhibit excellent physicochemical properties, including thermal durability, chemical resistance, electrical insulation, low transmission losses, gas barrier functionality, flame retardancy, and low friction. Therefore, a wide range of applications of these polymers are currently being developed. However, layering and metal plating with these materials is difficult, as they do not adhere easily to themselves or other materials. If layering and plating were possible, multiple applications in various fields could

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be realized. Examples of such applications include automobile-related electrical parts, such as car navigation systems and millimeter-wave radars, telecommunication devices, such as wireless and optical communication devices, and the millimeter-wave coaxial cables used in various fields, such as industrial device wiring and connection. The relative dielectric constant (ε_r) and dielectric loss tangent (tanδ) of PTFE are both low; hence, antennas and cables that use PTFE as the internal dielectric material present extremely low transmission losses. However, as PTFE is a low-adhesion material, the above issues remain during metal coating processes, such as copper film adhesion and metal plating on the PTFE surface.

On the basis of the background described above, the improvement of the adhesiveness of PTFE/plastic using a plasma hybrid process, metal plating technology, and its application to millimeter-wave devices are described here.

Atmospheric-pressure plasma graft polymerization (also called "atmospheric-pressure plasma hybrid surface treatment") [1–8], which has been developed by the group of the author, is presented as an innovative surface treatment method to improve the PTFE adhesiveness and enable surface plating with minimal impact on the environment.

In Sect. 2 of this chapter, the applicability of PTFE/plastics to millimeter-wave devices is briefly described, while Sect. 3 presents the atmospheric-pressure plasma hybrid surface treatment that enables plating on PTFE. In Sect. 4, methods to assess the effect of the surface treatment on PTFE metal plating are described. Finally, Sect. 5 describes several examples of improved strength of fiber-reinforced composite materials, which have a low dielectric constant similar to that of PTFE and can be used in radar domes. Some trial production results using this plasma hybrid surface treatment technology are also provided. Long-term durable adhesion properties of the surface are improved by this type of plasma treatments [9–29].

2 Applicability of PTFE/Plastics in Millimeter-Wave Devices

2.1 Plastic Properties: Dielectric Constant, Dielectric Loss Tangent, and Hydrophobicity

Figure 1 shows the dielectric constant (ε) and dielectric loss tangent (tanδ) of various plastics [30, 31]. Fluoroplastics, such as PTFE, PFA, and PCTFE, present the smallest dielectric constants and dielectric loss tangents among them. Liquid crystal polymers (LCPs) exhibit also similarly small values. In other words, these plastics exhibit low transmission losses when used as electronic substrates. The application of PTFE to millimeter-wave antennas is very promising and a particularly desired goal. As the era of next-generation 5G mobile telecommunication systems and automatic driving operations using millimeter-wave devices approaches, a paradigm change is also occurring in substrate materials for wireless communication devices, where the transition from conventional glass epoxy substrates and polyimide substrates to low-transmission-loss

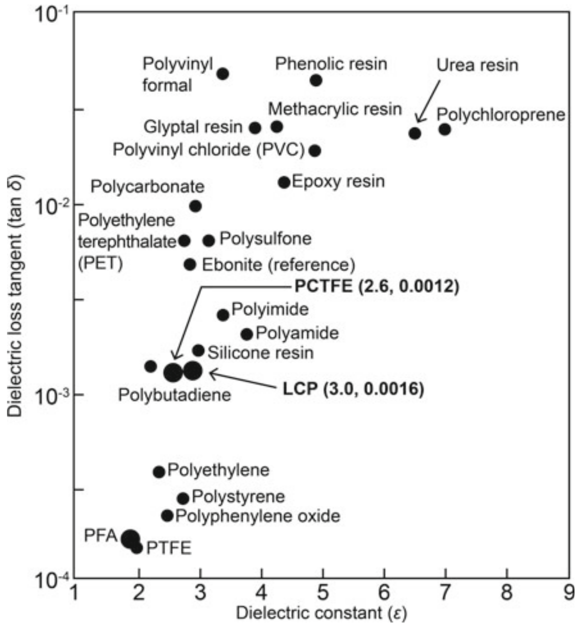


Fig. 1 Relation between dielectric constant and dielectric loss tangent of various plastics. Data are added to graphs in Refs. [3, 4]

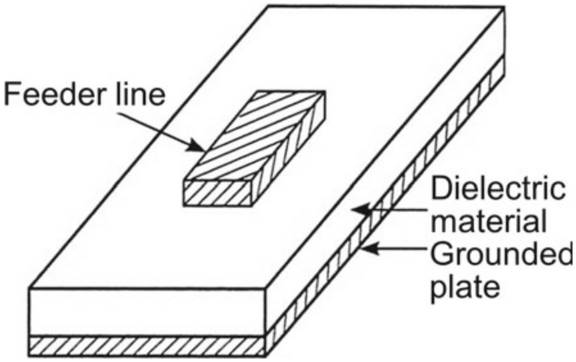
materials, such as LCPs and fluoroplastics, is occurring at a fast pace [32]. The latter materials are hydrophobic and hence biologically compatible with the human body, which allows for their application in implantable electronic devices.

2.2 Small-Size/High-Performance Millimeter-Wave Band Antennas

Developed examples of antennas for automobile radars using PTFE and LCPs are introduced according to Ref. [33]. Fujitsu Ten Ltd. (Now, Denso Ten Ltd.) has been continuously developing radars for automobiles using the millimeter-wave band at 30–300 GHz. Important electrical parts are the flat tri-plate antennas installed in automobiles and simple microstrip antennas. The flat antenna is indispensable to simultaneously realize automobile mountability and scanning functions. Moreover, microstrip antennas, with their simple structure, are particularly effective for cost reduction. However, as microstrip antennas contain a plastic substrate, the transmission losses are high, which reduces their efficiency.

Figure 2 schematically shows an example of a microstrip antenna structure. The microstrip antenna contains a dielectric plastic substrate that is interposed between a conductive feeder line and grounded plate (copper foil). To achieve high performance of the antenna, a thin dielectric material with a low relative dielectric constant is required. The microstrip antenna is also called a printed antenna, and it is constructed

Fig. 2 Structure of microstrip antenna



with dimensions matching the resonance frequency. This antenna is also a narrow-band, wide-beam antenna.

The electrical properties, mechanical strength, environmental durability, etc. of the plastic substrates of microstrip antennas have been studied in detail. When the antenna is used in the millimeter-wave band, its electrical properties are particularly important. As stated previously, the principal electrical properties of the substrate are its dielectric constant and dielectric loss tangent. Since the frequency bandwidth becomes narrower with the increasing dielectric constant, a dielectric constant of approximately three or smaller is usually appropriate. Uezato et al. [33] provides a description of the target materials LCPs and fluoroplastic PTFE. The results there show that the losses are lower with PTFE. Therefore, the possibility of realizing high-efficiency antennas using PTFE as the substrate material is a reality.

PTFE is a poorly adhesive material, and unresolved issues remain when a copper coating is attached to its surface. A thin adhesive layer of hydrophilic polyacrylic acid (thickness ~100 nm) is obtained when the atmospheric-pressure plasma hybrid treatment described in the next section is performed. Consequently, the above-described microstrip antenna could be potentially constructed by adhering a metal film to the polymer surface or by performing electroless plating, followed by electrolytic plating. Once this type of antenna is built, little deterioration of the electrical properties is expected as the polyacrylic acid layer interposed between the metal and dielectric material is very thin.

2.3 Applicability to High-Frequency Coaxial Cables

PTFE can be similarly applied to waveguides that supply microwaves or the following described coaxial cable assemblies with a high frequency corresponding to millimeter waves. Since both LCP and PTFE materials display low ε_r and tanδ, coaxial cables that use both materials as internal dielectrics exhibit extremely low transmission losses. Coaxial cables are used in a broad range of fields, including wireless and optical telecommunication systems, wiring and connection of industrial devices, and

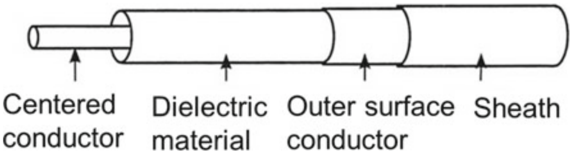


Fig. 3 Structure of coaxial electrical cable

automobile-related parts, such as car navigation systems and millimeter-wave radars [34]. In recent years, the applicable frequency bandwidth of coaxial cable assemblies has increased from several tens of GHz to several hundreds of GHz, and the bandwidth continues to widen. In response to these developments, high-frequency coaxial cable assemblies for millimeter-waves using porous PTFE as the dielectric material are already being commercialized [34].

The structure of an ordinary coaxial electrical cable is shown in Fig. 3. When poorly adhesive PTFE is used as the dielectric material, a copper coating or copper braided wire is used as the external dielectric material, but the dielectric material and metal do not adhere well to each other. Therefore, a surface treatment is needed. As shown in the figure, the cable is composed of a central conductor, such as a silver-plated copper wire; a dielectric material, such as porous PTFE; an outer-surface conductor, such as a silver-plated copper foil roll or silver-plated copper braided wire; and a sheath, such as fluorinated ethylene propylene (FEP). The processes listed below are normally used to yield excellent characteristics. Porous PTFE, the plastic material with the smallest tanδ and ε_r values is typically used. Furthermore, a uniform dielectric material is laid in the longitudinal direction on both the external diameter and void fraction using the paste press-out method. In addition, the outer surface conductor is formed in a spiral roll of silver-plated tape, where the tape width and roll pitch are strategically customized to ensure smooth signal flow. For low attenuation, silver-plated copper with low resistivity and porous PTFE with low dielectric constant and dielectric loss tangent are used.

However, as PTFE is a poorly adhesive material, certain problems remain to realize high-performance coaxial cables when a copper plating layer is deposited on its surface. Therefore, a thin adhesive layer of hydrophilic polyacrylic acid (thickness ~100 nm) can be laid on the surface of PTFE using the atmospheric-pressure plasma hybrid treatment described in Sect. 3. Upon adhering a metal film to the surface or performing electroless plating, followed by electrolytic plating, a high-performance coaxial cable can be built. Once this is accomplished, negligible deterioration of the electrical properties is expected, similar to the case of the microstrip antenna, because the polyacrylic acid layer inserted between the metal film and dielectric material is thin.

2.4 Applicability to Radomes

Section 5 describes the improvement of the strength of fiber-reinforced composite materials for aerospace applications through the atmospheric-pressure plasma graft

Fig. 4 Appearance of a radome at Osaka international airport

polymerization treatment. The word “radome” is a combination of two words: “radar” and “dome,” which are used to protect radar antennas from the natural environment, mainly from wind, rain, snow, etc., in airports or aircrafts themselves. Figure 4 shows an example of the outer appearance of a radome in an airport.

The use of a radome mitigates the effects of environmental conditions on the antenna system. Specifically, it provides wind speed, rain, and sunlight resistance. Therefore, deterioration of the antenna system over time can be minimized, without the need for adding reinforcements. Therefore, the antenna systems can be used safely over longer terms [35]. The materials used for radomes include glass fiber, PTFE, and fiber-reinforced composite materials, which allow radiowaves to pass through easily. Moreover, the electrical properties can be customized for the frequency band used. In addition, the land radomes placed at airports are actually buildings and have access doors, lightning rods, aircraft obstacle lights, etc.

Assuming that the radome is the final applied product, the section introduces several attempts to improve the strength of fiber-reinforced composite materials. Some trial production results using such plasma hybrid surface treatment are described. The treatment is performed to either make the fiber fabric hydrophilic or to modify the surface for improved adhesiveness. This research will contribute to broaden the applicability of organic fiber-reinforced composite materials with low dielectric constants (~3) and high radiowave permeabilities in aerospace structure materials.

3 Atmospheric-Pressure Plasma Hybrid Surface Treatment Toward Metal Plating of PTFE

3.1 Effect of Plasma Surface Treatment and Plasma Graft Polymerization Treatment

Figure 5 shows an overview of the electrode system of the surface treatment device using atmospheric pressure plasma. An unsteady current, e.g., pulses, is applied between the positive and negative sharp tip electrodes under argon flow, forming a plasma flow or jet. A film of the targeted material sample is passed through the gap over which the plasma jet is ejected, whereby the surface of the film is treated. In this case, only the single-sided surface impinged by the jet is treated. The use of this method, the so-called gliding arc-discharge plasma method, for surface treatment is relatively new, but several plasma-generation products that use it exist already in the market. In this method, because a plasma jet is used, it is possible to treat a three-dimensional or large object. However, to treat a large surface area, it is necessary to consider whether to move the torch according to the size or shape of the treated surface or to employ multiple torches. It is noted that, compared to surface treatment with argon-gas or air plasma alone classified as “plasma solo surface treatment”, the present surface treatment under a monomer gas environment (e.g., acrylic acid) should be referred to as a “plasma hybrid surface treatment.”

In the treatment system shown in Fig. 5, polymer, glass, and metal surfaces can be treated by a “plasma solo surface treatment” without a monomer gas environment, and the surface of these materials frequently becomes markedly hydrophilic with improved adhesiveness. This is because high-energy electrons (~1–10 eV) generated

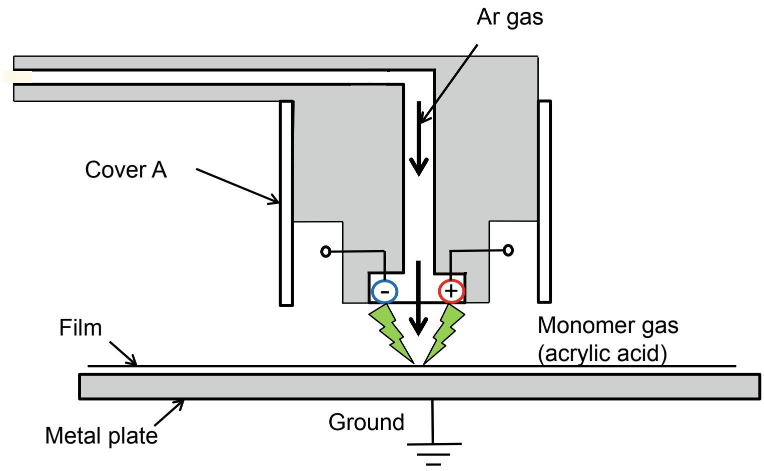


Fig. 5 Overview of electrode system of surface treatment device using atmospheric pressure plasma (Nozzle cover A is attached)

by electrical-discharge-induced atmospheric-pressure plasma induce the dissociation of the main and side chains on the material surface into radicals. Furthermore, the molecules of atmospheric gases, such as air and water, dissociate and generate radicals too. The electrons, radicals, and ions generated by the plasma are able to degrade organic materials such as the "dirt" (oils and fats) on the surface of materials. As a result, the surface becomes hydrophilic. However, owing to recombination reactions between radicals of the gas and on the surface, hydrophilic functional groups, such as hydroxyl (−OH), carbonyl (>C=O), and carboxyl (−COOH) moieties, are formed on the surface of the material. As a result of these phenomena, the surface becomes hydrophilic, the surface free energy increases, and it becomes easier to adhere or attach other materials to the surface.

However, if the treated materials are left in atmospheric air after the plasma solo surface treatment, the hydrophilic surface disappears almost completely within several days to one week, as the segments that include the functional groups burrow inside the plastic. In addition, plastic surfaces with low chemical reactivity, such as the surface of fluoroplastics like PTFE, barely become hydrophilic with such a plasma solo treatment.

Therefore, a treatment in which the effects of the plasma remain permanently without dissipating is highly desired. The "plasma hybrid surface treatment" has been proposed by the group of the author as such a method. Specifically, "plasma graft polymerization" is performed: monomers with unsaturated bonds (double bonds), such as acrylic acid CH_2=CHCOOH, are successively polymerized on the surface of the treated material activated by plasma irradiation, whereby a grafted functional film is formed. This permanent surface treatment method is typically used at reduced pressure below atmospheric pressure. However, the authors have also performed it with high efficiency using plasma at atmospheric pressure, establishing a new technology, "atmospheric-pressure plasma graft polymerization" [1–8, 36, 37]. A treatment system similar to that shown in Fig. 5 has been used for the present plasma treatment. Generally, permanent surface treatment methods in which a plasma treatment and a treatment with liquid chemicals, such as monomers or paint, are performed in parallel are referred to as "plasma hybrid surface treatments". The following text describes the principles, methods, and examples of atmospheric-pressure plasma graft polymerizations, a technology that can powerfully attach metal films to the surface of PTFE.

3.2 Principles of Atmospheric-Pressure Plasma Graft Polymerization and Adhesion Improvement

The principles of the present atmospheric-pressure plasma graft polymerization are summarized in the following reactions, using plasma graft polymerization of a hydrophilic monomer, in this case, acrylic acid, as an example of a double-bonded monomer.

Atmospheric-pressure plasma application (radical generation on the surface of fluoroplastics by plasma-induced electrons)

$$R-F \rightarrow R\cdot + F\cdot \tag{1}$$

$$R\cdot + CH_2 = CHCOOH \rightarrow R{-}CH_2{-}C\cdot HCOOH \tag{2}$$

Graft polymerization (hydrophilic layer formation)

$$R\cdot + nCH_2 = CHCOOH \rightarrow R{-}(CH_2{-}CHCOOH)_n{-} \tag{3}$$

where R represents the main chain of a fluoroplastic composed of C, H, O, and F atoms, and R·, F·, and R–CH_2–C·HCOOH are radicals with an unpaired electron. Although in reaction (1), cleavage of the C–C bonds in the main chain of PTFE is also possible, cleavage of the C–F bond occurs more frequently. The electrons generated by the atmospheric-pressure plasma (energy ~5 eV, electron number density ~10^{17} m^{-3}) collide with the monomer molecules, as well as the material surface, inducing the cleavage of covalent bonds and the formation of radicals. Finally, reaction (3) affords a hydrophilic graft polymerization layer of –R(CH_2–CHCOOH)$_n$ on the surface of the fluoroplastic R–F, which improves the adhesive properties of its surface.

In reduced-pressure plasma graft polymerization, which is the conventional technology, the energy of the generated electrons is relatively higher and the density is lower than the atmospheric-pressure plasma. Furthermore, to achieve a reduced-pressure environment, a vacuum chamber and vacuum pump are required for plasma generation. On the other hand, the authors have developed a method using atmospheric-pressure plasma by making use of high concentrations of generated radicals. This technology leads to high adhesion efficiency. Since the treatment can be performed at atmospheric pressure, it can be easily incorporated into manufacturing lines with high productivity. This treatment is also advantageous because it has a negligible impact on the environment, as it does not use harmful gases or solutions of heavy metals as in the case of the sodium-ammonia method.

3.3 Instrumentation Required for the Treatment

Figure 6 shows a schematic of the atmospheric-pressure plasma graft-polymerization treatment apparatus developed by the author's group, which can be used to treat an A4-size (210 × 297 mm) fluoroplastic film. Using this apparatus, the author has carried out sample treatment tests on a variety of polymers, metals, and glasses. The thickness of the sample is in the range of 300 μm–20 mm. The apparatus is placed inside the draft chamber shown in the figure with dotted lines. A single stainless evaporation vessel or double ones filled with the liquid acrylic acid monomer (FUJIFILM Wako Pure Chemical Industries, purity of 98 mass%) is placed on top of a plate heater equipped with a temperature regulator and a transformer as a steam generator inside the acrylic chamber. The monomer liquid is maintained at a constant temperature (~60 °C), and the monomer is vaporized inside the acrylic chamber, the

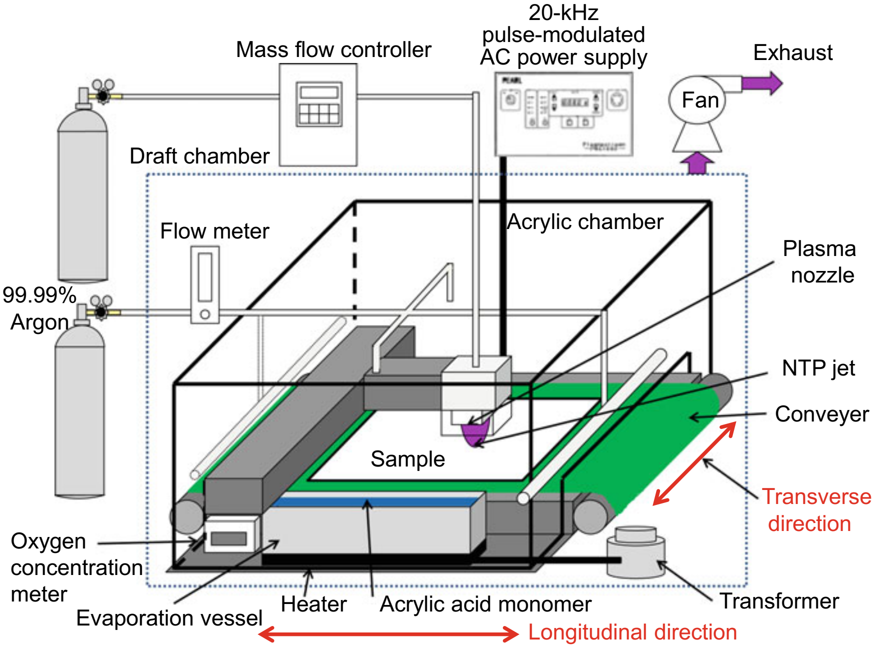
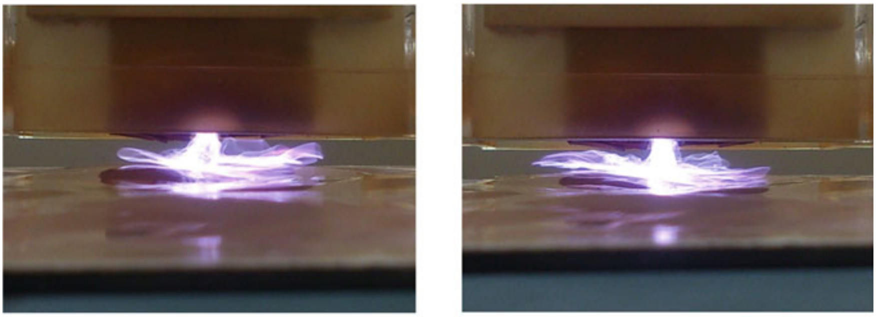
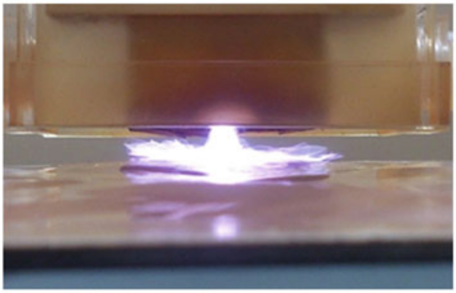


Fig. 6 Schematic of the atmospheric-pressure plasma graft-polymerization treatment apparatus

concentration of which is approximately 2000 ppm. Industrial argon with purity of 99.99% is used as the plasma-forming gas, and the argon flow in the plasma torch is regulated at a constant flow rate of *Q*. In later experiments, *Q* is changed from 30 to 50 L/min to know the effect of it. As shown in Fig. 5, a pair of sharp tip wire electrodes is located inside the plasma torch. When a pulse-modulated AC high-voltage (20 kHz and 24 kV) is applied, a gliding arc discharge is generated. The atmospheric-pressure low-temperature plasma jet formed by the s gas discharge the temperature of which is below 80 °C acts on the film sample surface on top of the conveyor to initiate the surface treatment. Graft polymerization is performed in an argon and acrylic acid steam environment, with the plasma radicalizing the flow while simultaneously cleaving the C−F bonds on the surface. The characteristic of this method is that the acrylic acid steam is ionized and a green colored plasma jet is generated. The plasma torch moves in the lateral direction as the sample is transported by the conveyor in the longitudinal direction. The whole surface of the A4-size film is treated. In order to place the plasma torch under a positive pressure argon environment, the argon gas also flows into the acrylic chamber. Moreover, to prevent air from flowing in through the entrance and exit of the film conveyor, gas injection-type curtains are generated at the entrance and exit. The total flow rate *q* of the flows in the chamber and gas flow curtains is 20 L/min. Furthermore, the chamber has to be thoroughly purged with argon gas before the experiment to remove any air inside the acrylic chamber.



(a) $Q = 30$ L/min (b) $Q = 40$ L/min



(c) $Q = 50$ L/min

Fig. 7 Photographs of plasma jets at varying flow rates of argon gas

3.4 *Effect of Gas Flow Rate on the Treatment*

Figure 7 shows photographs of the plasma jets at varying flow rates of argon gas. The figure shows a side-image during the film treatment. The gap between the torch and the film surface is 10 mm. As the flow rate increases, the plasma jet becomes longer. Observation of the plasma under these conditions reveals that the level of contact between the plasma and film surface is low at $Q = 30$ L/min and the highest at $Q = 50$ L/min. The adhesive properties are the greatest at $Q = 40$ L/min, as explained in more detail later. A stable and uniform monomer environment is formed by selecting the optimal flow rate, and stable, large adhesion is successfully achieved. The color change observed on the fluoroplastic surface during the sodium-ammonia treatment, i.e., the conventional surface treatment technology, does not occur in the present plasma treatment.

4 Surface Treatment Assessment and Technology for PTFE Metal Plating

4.1 Contact Angle Measurement

To evaluate the surface hydrophilicity of the treated fluoroplastic films, the contact angle can be measured with a measurement device (Kyowa Interface Science, CA-VE) after adding a 5 μL drop of purified water to the surface. Smaller contact angles indicate more hydrophilic surfaces. As an example, the contact angles of untreated films of PFA, PTFE, and PCTFE are large at 94°, 104°, and 91°, respectively; hence, those surfaces are hydrophobic. After treating those surfaces in a laboratory prototype plasma hybrid surface treatment apparatus, the contact angles decrease considerably, becoming 44° for PFA and 39° for PTFE (one second after dropping the water droplet). Interestingly, the contact angle rapidly decreases with time: in the case of PTFE, it drops to 17° in 2 min and reaches saturation at just 10°; that is, the surface becomes superhydrophilic.

4.2 T-type Peeling Test Method and Results

The surface of a highly pure PTFE sample is subjected to the previously described surface treatment. After adhering a 25-mm-wide stainless-steel plate to the treated sample using a 2-part epoxy adhesive (Konishi E-set), the adhesive strength is evaluated by performing a T-type peeling test. A peeling-test machine (digital force gauge plus electrical measurement stand ZTA-100 N + MX2-500 N, Imada Co., Ltd., Japan) is used in this T-type (90°) peeling test. A piece of a non-adhesive sample is placed in a clamp, the stainless-steel plate is fastened by a jig, and allowed to slide from left to right, while the tension angle is maintained at 90°. The peeling strength or adhesive strength is measured while the test piece is peeled by pulling upward at a peeling speed of 100 mm/min. The sample is layered in the following order: PTFE film/plasma graft polymerization layer/epoxy adhesive layer/stainless-steel metal plate. It can thus be confirmed that there is sufficiently large adhesive force between the plasma graft polymerization layer and epoxy adhesive layer and between the epoxy adhesive layer and stainless-steel metal plate layer. Therefore, peeling is observed to occur mainly at the interface of PTFE/graft polymerization layer.

The results of the T-type peeling test are described below. PTFE (thickness 0.2 mm) is treated by nonthermal plasma graft polymerization at an argon main flow rate of 30, 40, or 50 L/min, an acrylic acid temperature of 60 °C, and a head feed rate of 4 mm/s, and the T-type peeling test is then performed to measure the adhesive strength. The peeling test is typically performed six times at each flow rate. The results show that the maximum adhesive strength for a width of 25 mm is 45.3 N at 30 L/min, 65.0 N at 40 L/min, and 57.5 N at 50 L/min. Furthermore, the average

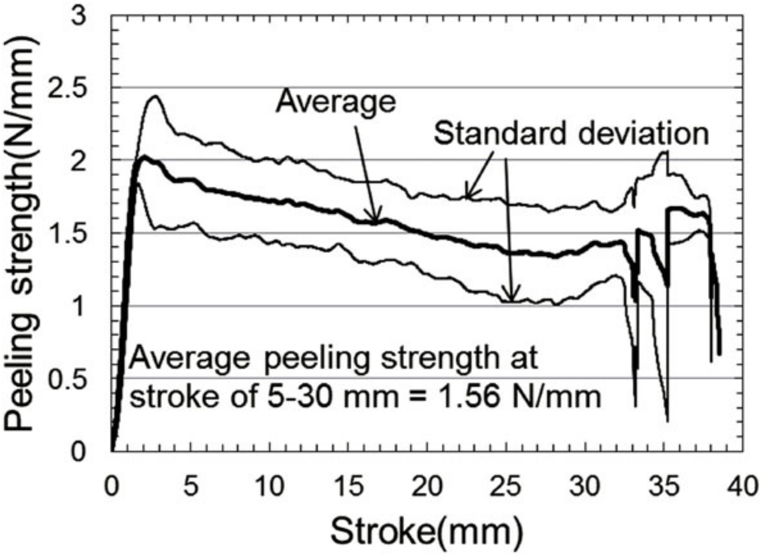


Fig. 8 Measurement results of the curve of stroke–strength at a flow rate of 40 L/min. Maximum average peeling strength for six samples is 2.0 N/mm

adhesive strength for a width of 25 mm is recorded as 20.3 N at 30 L/min, 45.3 N at 40 L/min, and 26.8 N at 50 L/min. In other words, the maximum and average adhesive strengths are both observed at 40 L/min.

Figure 8 shows the measurement results of the curve of stroke–strength at a flow rate of 40 L/min [2]. The number of samples is six, and the three curves in the graph represent the average value and average value plus and minus standard deviation (±SD). The unit of N/25 mm on the vertical axis represents the peeling strength for a width of 25 mm, where N denotes the unit Newton. Although the variation in the data is somewhat large, a maximum adhesive strength of 2.0 N or more per 1 mm of width and an average adhesive strength of 1.56 N per 1 mm of width are observed. This adhesive strength is very high, and it could not have been achieved without using a sodium solution solvent surface treatment agent, which is the conventional technology. The best results for both the maximum and average adhesive strengths are obtained at a flow rate of 40 L/min. The reason for this is discussed below. First, when the flow rate is low, plasma jet injection and the activation of the monomer or PTFE surface are insufficient, resulting in low adhesive strength. When the flow rate is high, the monomer concentration is diluted or the plasma energy for the unit gas flow rate is low, causing a reduction in the adhesive strength. Thus, the peak strength is observed at $Q = 40$ L/min. Based on these results, we can conclude that PTFE adhesiveness is markedly improved by performing plasma graft-polymerization in a highly concentrated acrylic acid environment using a corona discharge plasma device.

The maximum peeling strength or adhesive strength (value for a width of 25 mm) achieved previously for PTFE—stainless steel materials is shown in Table 1. The

Table 1 Maximum peeling strength of T-type peeling strength for three-types of fluoropolymer plastics (Use of acrylic acid, value for sample width 25 mm, maximum values until April 1, 2018)

	Untreated	Ar plasma solo treatment	Plasma graft-polymerization treatment
PTFE	Lower than 0.3	6.7	65.0
PFA	Lower than 0.6	–	50.0
PCTFE	Lower than 0.6	–	35.5

maximum peeling strength is determined from the maximum load point in the elongation—peeling strength diagram. It is known that the adhesiveness of fluoroplastics, unlike other polymer materials, does not increase much after a plasma solo treatment. However, if the conditions are suitable, the adhesiveness increases to a certain degree, e.g., 6.7 N in the case of PTFE. The peeling strength for untreated PTFE, PFA, and PCTFE is up to 0.3, 0.6, and 0.6 N, respectively; hence, adhesion is difficult. Furthermore, upon plasma graft polymerization treatment, the peeling strength is very high, 65.0, 50.0, and 35.5 N, respectively. It is concluded from these results that the peeling strength or adhesive strength is sufficient to enable applications for fluoroplastic endoscopes, chemical liquid injection tubes, and electronic substrates.

4.3 *Method of Copper Plating on PTFE and Results*

Through trial and error, we have successfully used the sensitizing–activating method to perform electroless copper-plating on the surface of PTFE films treated by atmospheric-pressure plasma graft polymerization [3]. The specific procedures are described below.

(1) Sensitizing process: The plasma graft polymerized PTFE film is immersed for 5 min in a mixed aqueous solution containing 20–40 g/L $SnCl_2$ and 20–40 mL/L HCl, after which it is washed with purified water.

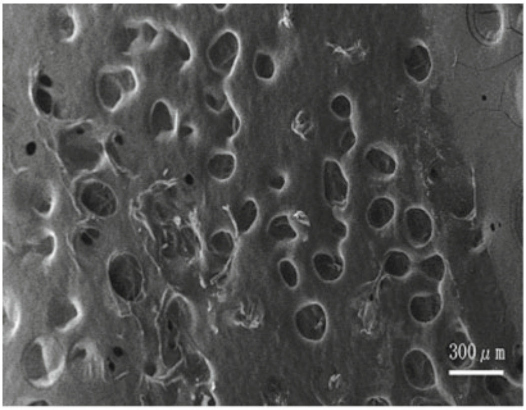
(2) Activation process: The film is immersed for 5 min in a mixed aqueous solution containing 0.25–0.50 g/L $PdCl_2$ and 2.5–5.0 mL/L HCl, after which it is washed with purified water.

(3) Alkaline cleaning process: To remove the tin on the film and metalize it with palladium, cleaning with an alkaline solution is performed. Specifically, the film is immersed in 10% NaOH at room temperature for 10 min and washed again with purified water. When the treated film is immersed in NaOH for an extended period of time, the polyacrylic acid polymerized layer begins to peel off and the process fails.

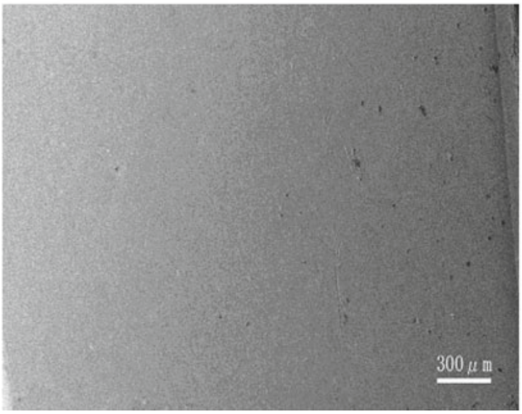
(4) Electroless plating process: After finishing the palladium metallization, the sample is immersed for 3 min in a copper-plating solution (concentration of $CuSO_4 = 3.5$ g/L, Rochelle salt $KNaC_4H_4O_6{\cdot}4H_2O = 34$ g/L, $Na_2CO_3 = 3.0$ g/L, $NaOH = 7.0$ g/L, and 37% formalin $HCHO = 13$ mL/L) under stirring.

Then, it is washed with purified water and dried. To increase the thickness of the metal plating, electrical plating can be performed after the electroless plating procedure.

Figure 9a and b show SEM images of copper plating on untreated and treated PTFE film surfaces (Nikon E − SEM2700 is used), respectively. Many holes with a diameter of 100–200 μm are observed on the surface of the untreated sample, as a result of the formation of bubbles caused by the hydrophobicity of the surface. In this case, uniform metal plating is impossible. Figure 9b shows the very smooth metal-plated surface obtained for the treated film, where none of the holes in Fig. 9a are observed.



(a) copper plating for untreated PTFE film



(b) copper plating for plasma graft polymerization treated PTFE film

Fig. 9 SEM images of untreated and treated PTFE film surface copper plating

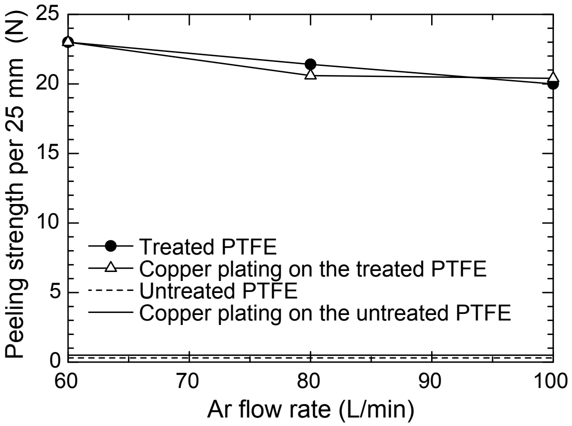


Fig. 10 Example of results for T-type peeling tests for metal plating layers on treated and untreated PTFE films (the effect of argon gas flow rates in plasma graft polymerization on the peeling strength)

Electroless copper plating can be performed on four types of PTFE-treated/untreated samples. Figure 10 shows the results when a stainless-steel plate is adhered to the surface of one of these samples during the previously described T-type peeling test. The horizontal axis shows the argon gas flow rate. The peeling strength or adhesive strength of the untreated sample is less than 0.5 N in the figure, while the maximum peeling strength or adhesive strength for a treated sample is 23 N. This value is large and approximately 50 times larger than that of the untreated sample. The thermal durability at 300 °C and 1 min of the copper plating was also confirmed.

4.4 Method of Nickel Plating on PTFE and Results

Through trial and error, we successfully used the catalyzer–accelerator method to perform electroless nickel plating on a PTFE film treated by the atmospheric-pressure plasma graft polymerization [6]. The specific procedure consists of the following processes.

(1) Activation process: The film is immersed in Kondilizer FR Konku (concentration = 50 mL/L), a chemical that improves the adherence of catalysts, for 5 min at 40 °C, after which it is washed with purified water.

(2) Catalyzer process: A catalyzation treatment is performed with a mixed colloidal solution of Sn^{2+} and Pd^{2+}. The temperature of the solution is 35 °C with a sintering time of 6 min. Then, the film is washed with purified water.

(3) Accelerator process: After immersing the film in an accelerator solution (an acidic solution with concentration of 200 mL/L) at a constant temperature for 5 min, it is washed with purified water.

(4) Electroless plating process: The film is immersed in an acidic nickel-plating solution (Top Nikoron TOM−S, concentration = 200 mL/L). The temperature of the liquid is 80 °C. After that, it is washed with purified water and dried. To

increase the thickness of the metal plating, electrical plating can be performed after electroless metal plating.

Figure 11 shows photographs of a sample in which the aforementioned process is used to perform nickel electroless plating on the surface of PTFE untreated and treated by plasma graft polymerization. Although no metal plating occurred on the

Fig. 11 Photographs of samples of nickel electroless plating on the surface of PTFE untreated and treated by plasma graft polymerization (sample width of 10 cm)

(a) untreated surface

(b) plasma treated surface

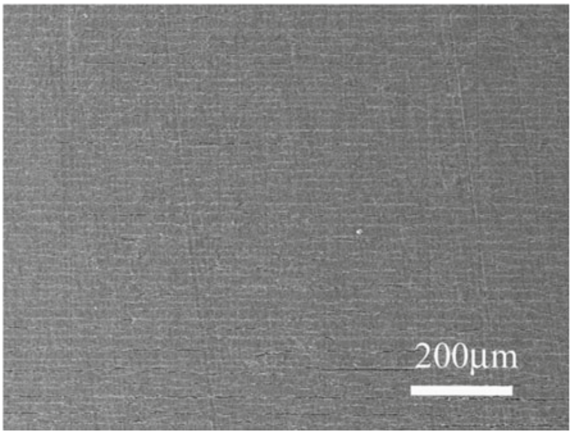


Fig. 12 Results of cyclic bending test of nickel plated PTFE (SEM image after test)

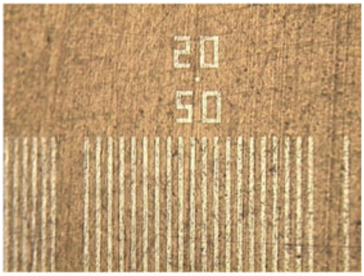
surface of untreated PTFE, a uniform plating film is formed after treatment. The peeling strength or adhesive strength reaches over 1 N per 1 mm width.

To test the flexibility of the metal-plated PTFE film, a repeated bending test is performed using a repeated bending tester. Accordingly, 100,000 rounds of bending at a bending angle of approximately 170° are performed on the metal-plated PTFE film sample. The sample is held by a rod for bending and two sample holding rods. Figure 12 shows a SEM image after the test at an argon flow rate of 40 L/min. The adhesiveness of the metal plating is fairly good with no peeling observed.

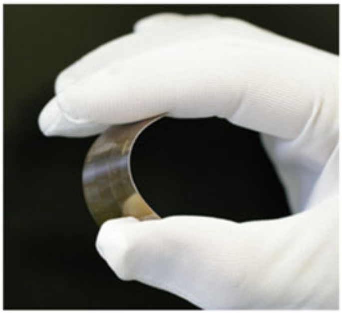
4.5 Microfabrication of Nickel Plating on PTFE

Pattern generation by photolithography on nickel-plated PTFE can be performed according to the following processes.

(1) The sample is attached to a Si wafer with a diameter of 4 inch.
(2) A positive-type resist (OFPR-800 50cP, Tokyo Ohka Kogyo Co., Ltd., Japan) is coated on the surface by a spin-coating process (first time: 500 rpm, 5 s; second time: 4000 rpm, 20 s). The thickness of the film on the Si substrate is typically 1.2–1.5 μm.
(3) Pre-baking of the sample is performed in an oven at 90 °C for 15 min.
(4) Mask exposure is performed at 18 mW/cm^2 for 20 s using an extra-high-pressure mercury lamp.
(5) The resist and nickel at the unexposed parts are dissolved using a developer liquid (tetramethyl ammonium hydroxide, NMD−3, 2.38%, Tokyo Ohka Kogyo Co., Ltd.) for 45 s.
(6) The wafer is washed with flowing purified water for 2 min. The resist is completely removed.
(7) After blowing with nitrogen gas, the wafer is dried in an oven at 90 °C for 10 min.



(a) Photolithographic pattern formed on nickel plated PTFE



(b) Confirmation of the flexibility of PTFE having a photolithographic pattern formed thereon

Fig. 13 Photolithography of nickel plating of PTFE by atmospheric pressure plasma polymerization

Figure 13a shows an example of this procedure. The numbers 20 and 50 shown in the photograph in the figure indicate that each line is drawn at a thickness of 20 μm and intervals of 50 μm. As shown in Fig. 13b, the PTFE on which the photolithography pattern is created exhibits flexibility, and applications such as flexible print boards or GHz-bandwidth high-frequency antennas may thus be expected.

5 Plasma Hybrid Surface Treatment of Fiber-Reinforced Composite Materials

5.1 Adhesion of Fiber-Reinforced Composite Materials

A surface modification/adhesion improvement assessment can be performed on fiber-reinforced composite materials with different dielectric constants, aiming for applications in radome structures [36, 37]. In this study, plain weave fabrics made of the following four types of organic fibers were used as samples: polypropylene (PP) fiber Innegra (Integrity Corporation), polyethylene (PE) fiber Dyneema

(Toyobo Co., LTD.), polyarylate (PAR) fiber Vectran (Kurary Co., LTD.), and poly *p*-phenylenebenzo bisoxazole (PBO) fiber Zylon (Toyobo Co., LTD.).

The device and apparatus are similar to those shown in Figs. 5 and 6. An A4 size (approximately 300 mm × 200 mm) sample is fixed to a conveyor belt of an atmospheric-pressure plasma graft polymerization apparatus, and while the plasma torch moves horizontally at a speed of 4 mm/s, a pulse modulated AC argon plasma jet (frequency 20 kHz; voltage 24 kV; pulse modulation frequency 60 Hz; pulse duty ratio 99%; gas flow rate 30 L/min) is sprayed on the surface. At that time, argon (flow-rate of 3 L/min) bubbling in an acrylic acid monomer solution heated to 45 °C is sprayed from the side of the jet and, as the surface of the test material is radicalized, the carbon bonds are cleaved, and graft polymerization occurs. After the torch makes a roundtrip, the test material is moved vertically 10 mm through the conveyor belt, and this is repeated to treat the entire A4 size surface.

First, to evaluate the adhesiveness, a peeling test is performed on each of the materials, Cyneema, Vectran, and Zylon, which are either treated or untreated by plasma graft polymerization. A 50-mm-long part of the test sample extracted at a width of 25 mm and length of 100 mm is adhered to an aluminum plate coated with epoxy adhesive (Konishi E-set) at a thickness of 250 μm, and the adhesive is cured by allowing it to rest at room temperature (~25 °C) for 24 h under a load of 5 N. Subsequently, the aluminum plate is peeled at a speed of 100 mm/min, and the peeling strength (adhesive strength) at that time is measured.

Subsequently, the vacuum-assisted resin transfer molding (VaRTM) method [38] can be used to trial-produce flat fiber-reinforced composite material test pieces using treated or untreated samples by the following method. For the thickness to be approximately 2 mm, the test materials are layered with 6 fibers (Innegra), 10 fibers (Dyneema), 8 fibers (Vectran), and 12 fibers (Zylon) and, after immersion in a matrix resin by vacuum aspiration, the materials are heated and the resin is cured. Epoxy resin (XNR6815/XNH6815, Nagase ChemteX Corporation) is used as the matrix resin. The resin curing temperature and time are 80 °C and 2 h. Three test pieces (length × width for peeling test: 250 mm × 25 mm, for compression test: 80 mm × 12.7 mm, for three-point bending test: 90 mm × 12.7 mm) are obtained by cutting the fiber-reinforced composite material test pieces. A peeling test (ASTM D3039), a compression test (SCAMA SRM 1R-94), and a three-point bending test (ASTM D790) are performed at room temperature using a material universal test machine (AUTOGRAPH DCS-10 T, Shimadzu Corporation) at speeds of 2, 1, and 1 mm/min, respectively.

5.2 Results and Discussion

The results of the peeling tests for the test materials are shown in Fig. 14. It is found that the peeling strength, σ_T, increases after nonthermal plasma graft polymerization of all the test materials. However, as shown in Fig. 15, σ_T tends to decrease in the peeling test for the fiber-reinforced composite material specimen. It is considered

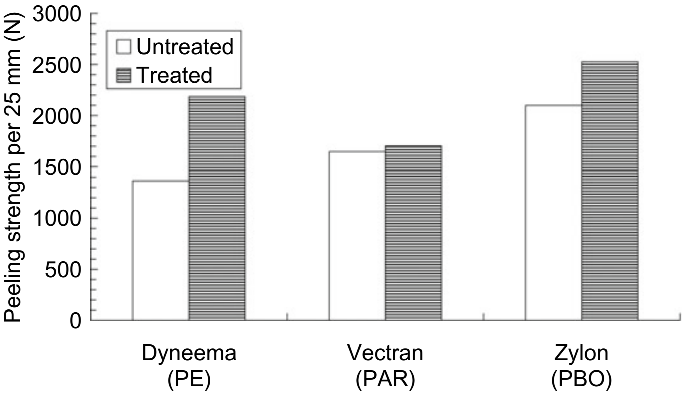


Fig. 14 Results of peeling tests for three types of fiber-reinforced composite material specimens [36]

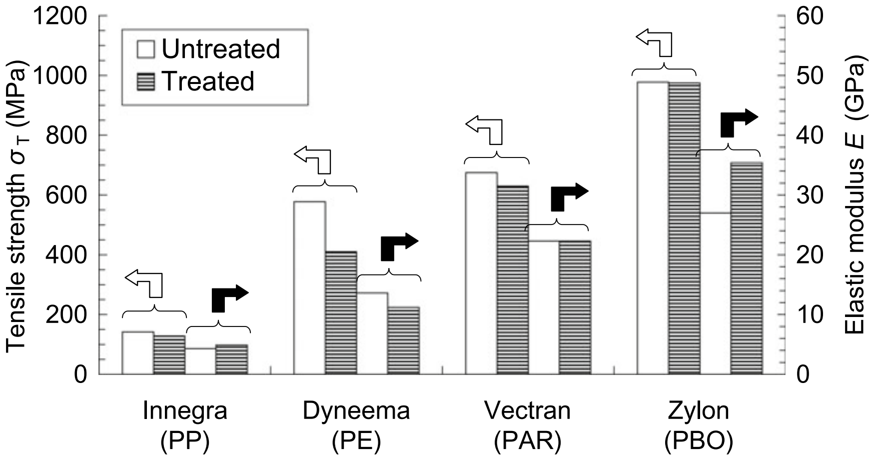


Fig. 15 Result of tensile tests for four types of fiber-reinforced composite material specimens [36]

that slight damage to the fiber surface during the plasma treatment may reduce σ_T. In particular, the Dyneema sample shows a lower heat resistance than that of the other tested materials, which is easily influenced by the temperature (~150 °C) during plasma irradiation; therefore, it is much smaller than that of the other tested materials. With regard to the elastic modulus, E, the relationship between the adhesion improvement by the plasma treatment and the fiber damage is different. In particular, the Dyneema sample, which has a lower heat resistance, presents a large degree of fiber damage; therefore, E decreases. In contrast, the Zylon material, which has a higher heat resistance, presents negligible fiber damage; thus, E is improved.

On the other hand, in the compression test, as shown in Fig. 16, the compression strength, σ_c, is improved in all the composite materials. It is considered that

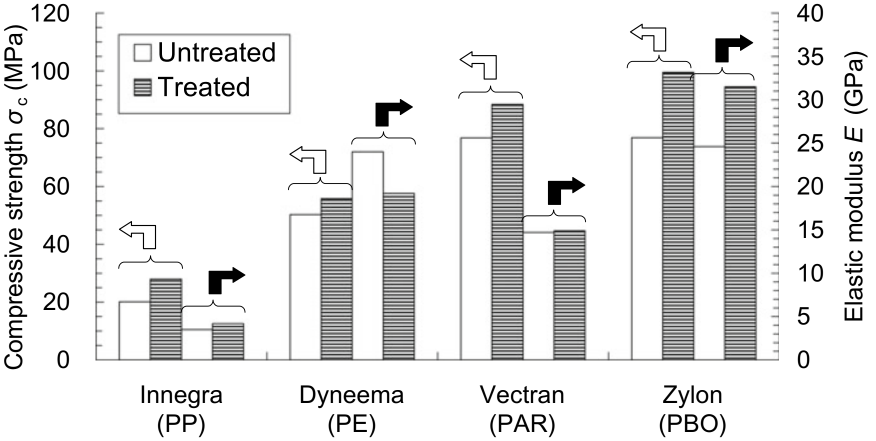


Fig. 16 Results of compression tests for four types of fiber-reinforced composite material specimens [36]

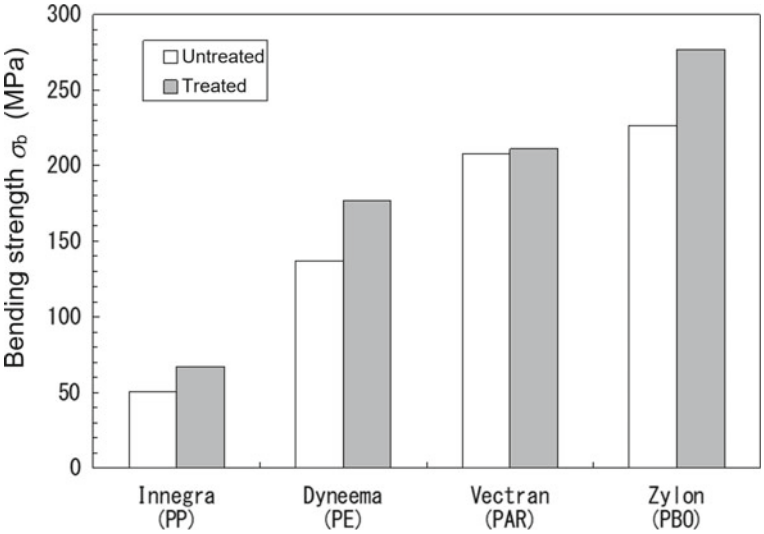


Fig. 17 Results of bending tests for four types of fiber-reinforced composite material specimens

σ_c is improved because of an enhancement of the adhesion after plasma graft polymerization. With regard to E, similar results to those of the peeling test are obtained. Furthermore, Fig. 17 shows a result of bending test for four-types of fiber-reinforced composite material specimens. In the bending test, an increase in the bending strength, σ_b, is observed. This increase is believed to be caused by an improvement of the compression strength, particularly during the plasma graft polymerization treatment.

6 Conclusion

The improvement of the adhesion and plating technology on PTFE and plastics treated by the plasma hybrid process, its application to millimeter-wave device, and its feasibility have been thoroughly discussed. The atmospheric-pressure plasma graft polymerization process developed by us has been employed for improvement of fluorocarbon plastic adhesion, followed by metal plating of PTFE. The fundamentals of plasma treatment, examples of electrode systems, the apparatus for plasma treatment, the effects of the surface treatment, plating methods on PTFE, and evaluation of the plasma composite surface treatment on fiber-reinforced composite materials have also been described.

With regard to surface modification of PTFE and improvement of adhesion, the adhesive strength obtained by the conventional technology, i.e., the sodium-based solution surface treatment method, can be significantly surpassed upon further optimization of the treatment conditions, improvement of wide electrodes, and other approaches. We believe that it would be possible to realize a targeted value of 5 N per 1 mm width, which is the standard value for the sodium solution method, while averting the color change of the fluorocarbon plastic.

Among our achievements, the peeling strength of 2 N per 1 mm of sample width or more, which is realized with a fluorocarbon polymer, is the highest among the various methods to improve the fluorocarbon polymer adhesion without surface color change. This highest peeling strength has been confirmed by researchers at a major company in Japan manufacturing medical devices made of fluorocarbon polymers. In the future, we will develop plasma hybrid surface treatments for electronic parts such as coaxial cables, antennas, and reinforcing fibers. We would like to increase the adhesive strength even further, the number of successful cases using this developed method, and promote and industrialize such plasma hybrid surface treatment. If the opportunity arises, we would like to be involved in collaborative research toward a wide range of applications. Furthermore, we intend to develop a roll-to-roll large-area treatment apparatus and pursue aerospace applications.

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References

1. Okubo, M., Tahara, M., Saeki, N., Yamamoto, T.: Surface modification of fluorocarbon polymer films for improved adhesion using atmospheric-pressure nonthermal plasma graft-polymerization. Thin Solid Films, Elsevier **516**(19), 6592–6597 (2008)
2. Hori, K., Fujimoto, S., Togashi, Y., Kuroki, T., Okubo, M.: Improvement in molecular-level adhesive strength of PTFE film treated by atmospheric plasma combined processing. IEEE Trans. Ind. Applicat. (2018). https://doi.org/10.1109/TIA.2018.2868035
3. Okubo, M., Tahara, M., Kuroki, T., Hibino, T., Saeki, N.: Plating technology for fluorocarbon polymer films using atmospheric-pressure nonthermal plasma graft polymerization. J. Photopolymer Sci. Tech. **21**, 219–224 (2008)
4. Okubo, M., Tahara, M., Aburatani, Y., Kuroki, T., Hibino, T.: Preparation of PTFE film with adhesive surface treated by atmospheric-pressure nonthermal plasma graft polymerization. IEEE Trans. Ind. Applicat. **46**(5), 1715–1721 (2010)
5. Feng, Z., Saeki, N., Kuroki, T., Tahara, M., Okubo, M.: Surface modification by nonthermal plasma induced by using magnetic-field-assisted gliding arc discharge, Appl. Phys. Lett. **101**, 041602 (2012)
6. Kuroki, T., Tahara, M., Kuwahara, T., Okubo, M.: Microfabrication and metal plating technologies on polytetrafluoroethylene film surface treated by atmospheric-pressure nonthermal-plasma graft polymerization process. IEEE Trans. Ind. Applicat. **50**(1), 45–50 (2014)
7. Kuroki, T., Nakayama, K., Nakamura, D., Onji, T., Okubo, M.: Nonthermal plasma hybrid process for preparation of organic electro-luminescence fluoropolymer film devices. IEEE Trans. Ind. Applicat. **51**(3), 2497–2503 (2015)
8. Okubo, M., Onji, T., Kuroki, T., Nakano, H., Yao, E., Tahara, M.: Molecular-level reinforced adhesion between rubber and PTFE film treated by atmospheric plasma polymerization, Plasma Chem. Plasma P. **36**, 1431−1448 (2016)
9. Latini, G., Tan, L.W., Cacialli, F., Silva, S.R.P.: Superficial fluoropolymer layers for efficient light-emitting diodes. Org. Electron. **13**(6), 992–998 (2012)
10. Wang, J.C., Karmakar, R.S., Lu, Y.J., Wu, M.C., Wei, K.C.: Nitrogen plasma surface modification of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) films to enhance the piezoresistive pressure-sensing properties, J. Phys. Chem. C, **120**(5), 25977−25984 (2016)
11. Tahara, M., Cuong, N.K., Nakashima, Y.: Improvement in adhesion of polyethylene by glow-discharge plasma. Surf. Coatings Technol. **174–175**, 826–830 (2003)
12. Cernáková, L., Kovácik, D., Zahoranová, A., Cernák, M., Mazúr, M.: Surface modification of polypropylene non-woven fabrics by atmospheric-pressure plasma activation followed by acrylic acid grafting. Plasma Chem. Plasma P. **25**(4) 427−437 (2005)
13. Wang, R., Zhang, C., Liu, X., Xie, Q., Yan, P., Shao, T.: Microsecond pulse driven Ar/CF_4 plasma jet for polymethylmethacrylate surface modification at atmospheric pressure. Appl. Surf. Sci. **328**, 509−515 (2015)
14. Ma, S., Zhang, X., Yu, B., Zhou, F.: Brushing up functional materials. NPG Asia Materials **11**, 24 (2019)
15. Griffin, M.F., Ibrahim, A., Seifalian, A.M., Butler, P.E.M., Kalaskar, D.M., Ferretti, P.: Argon plasma modification promotes adipose derived stem cells osteogenic and chondrogenic differentiation on nanocomposite polyurethane scaffolds; implications for skeletal tissue engineering. Mater. Sci. Eng. C **105**, 110085 (2019)
16. Savoji, H., Mohammadi, M.H., Rafatian, N., Toroghi, M.K., Wang, E.Y., Zhao, Y., Korolj, A., Ahadian, S., Radisic, M.: Cardiovascular disease models: a game changing paradigm in drug discovery and screening. Biomaterials **198**, 3–26 (2019)
17. Ohkubo, Y., Endo, K., Yamamura, K.: Adhesive-free adhesion between heat-assisted plasma-treated fluoropolymers (PTFE, PFA) and plasma-jet-treated polydimethylsiloxane (PDMS) and its application. Sci. Rep. **8**(1) (2018)

18. Schonhorn, H., Hansen, R.H.: Surface treatment of polymers for adhesive bonding. J. Appl. Polym. Sci. **11**(8), 1461–1474 (1967)
19. Miller, M.L., Postal, R.H., Sawyer, P.N., Martin, J.G., Kaplit, M.J.: Conditioning polytetrafluoroethylene surfaces for use in vascular prostheses. J. Appl. Polym. Sci. **14**(2), 257–266 (1970)
20. Marchesi, J.T., Keith, H.D., Garton, A.: Adhesion to sodium naphthalenide treated fluoropolymers. part iii. mechanism of adhesion. J. Adhes **39**(4), 185−205 (1992)
21. Inagaki, N., Yasuda, H.: Adhesion of glow discharge polymers to metals and polymers. J. Appl. Polym. Sci. **26**(10), 3333–3341 (1981)
22. Okubo, M., Saeki, N., Taguchi, T., Yamamoto, T.: Development of surface treatment apparatus for manufacturing functional wear using low-temperature plasma. Trans. J. Soc. Mech. Eng. Part A **72**(2), 263−268 (2006) (in Japanese)
23. Macedo, M.J.P., Silva, G.S., Feitor, M.C., Costa, T.H.C., Ito, E.N., Melo, J.D.D.: Surface modification of kapok fibers by cold plasma surface treatment. J. Mater. Res. Technol. **9**(2), 2467−2476 (2020)
24. Haji, A., Ashraf, S., Nasiriboroumand, M., Lievens, C.: Environmentally friendly surface treatment of wool fiber with plasma and chitosan for improved coloration with cochineal and safflower natural dyes. Fibers and Polym. **21**(4), 743−750 (2020)
25. Wang, W., Cai, X.: Polyglycerol-grafted multi-walled carbon nanotubes were prepared by one-pot method and reacted with folic acid to enhanced stability in a physiological medium. Compos. Interfaces **26**(11), 989–1000 (2019)
26. Amesimeku, J., Song, W., Wang, C.: Fabrication of electrically conductive and improved UV-resistant aramid fabric via bio-inspired polydopamine and graphene oxide coating. J. Text. Inst. **110**(10), 1484–1492 (2019)
27. Hedayati, M., Reynolds, M.M., Krapf, D., Kipper, M.J.: Nanostructured surfaces that mimic the vascular endothelial glycocalyx reduce blood protein adsorption and prevent fibrin network formation. ACS Appl. Mater. Interfaces **10**(38), 31892–31902 (2018)
28. Ge, R.-K., Wang, J.-W., Zhang, J., Ren, H.: UV-/moisture-curable silicone-modified poly(urethane–acrylate) adhesive for untreated PET substrate. Polym. Bull. **75**(8), 3445−3458 (2018)
29. Ohkubo, Y., Shibahara, M., Ishihara, K., Nagatani, A., Honda, K., Endo, K., Yamamura, K.: Effect of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated polytetrafluoroethylene (PTFE). J. Adhes. **95**(3), 242–257 (2019)
30. Yasuda, T.: Purasuchikkusu [Plastics], Kogyo Chosa Kai, 52(5), 79−84 (2001) (in Japanese)
31. Ando, S.: Fundamental properties of thermally stable and insulating polymeric materials: focusing on polyimides. Mater. Sci. Technol. **48**(5), 194−198 (2012) (in Japanese)
32. Raveendran, A., Sebastian, M.T., Raman, S.: Applications of microwave materials: a review. J. Electron. Mater. **48**(5), 2601–2634 (2019). https://doi.org/10.1007/s11664-019-07049-1
33. Uezato, Y., Yoshitake, H., Shono, M., Fujimoto, M., Yamawaki, T.: Compact and high-performance millimeter-wave antennas. Fujitsu Ten Tech. J. 36, 19−25 (2011) https://www.denso-ten.com/business/technicaljournal/pdf/36-3.pdf. (Accessed 04 May 2019)
34. Totoku Electric Co., Ltd., Coaxial cable assembly for microwave applications standard specification, https://www.totoku.com/product/highfrequency/microwave.html. (Accessed 04 May 2019)
35. Rosato, D., Rosato, D.: Plastics Engineered Product Design, Elsevier, pp. 198−343 (2003)
36. Aoi, T., Kuroki, T., Tahara, M., Okubo, M.: Improvement of strength characteristics of aerospace fiber reinforced composite materials using atmospheric pressure plasma-graft polymerization treatment. IEEJ Trans. FM. A **131**(5), 412−413 (2011) (in Japanese)

37. Aoi, T., Kuroki, T., Okubo, M.: Improving the strength of fiber reinforced composites for aerospace vehicles by atmospheric pressure plasma graft polymerization, Supervisor, M. Kogoma, *Taikiatsu Purazuma No Seiseiseigyo To Ouyo Gijyutsu (Kaiteiban) [Atmospheric Pressure Plasma Generation Control and Application Technology (Revised edition)]*, Chapter 3, Section 6, Science & Technology Co., Ltd., pp. 169−182 (2012) (in Japanese)
38. Kamae, T., Kochi, S., Wadahara, E., Shinoda, T., Yoshioka, K.: Advanced-VaRTM system for aircraft structures−material technologies. ICCM-17 Proc 9 (2009). http://iccm-central.org/Proceedings/ICCM17proceedings/papers/A2.9%20Kamae.pdf. (Accessed 21 Sep 2022)