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# Comparison between adhesion properties of adhesive bonding and adhesive-free adhesion for heat-assisted plasma-treated polytetrafluoroethylene (PTFE)

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**ABSTRACT**
Heating during plasma treatment, known as heat-assisted plasma treatment, has recently reported to positively affect the adhesion properties of polytetrafluoroethylene (PTFE). In the present study, the adhesion properties of adhesive bonding and adhesive-free adhesion were compared for plasma-treated PTFE with different plasma treatment times and with or without heating during the plasma treatment. The relations among adhesion strength, plasma treatment time, radical density ratio, surface morphology, and surface hardness were investigated. No correlation was found between the adhesion strength and the radical density ratio or between the adhesion strength and the oxygen-containing-functional-group ratio. In contrast, correlation was observed between the adhesion strength and the surface hardness. In addition, the heat-assisted plasma treatment time affected the recovery of the weak boundary layer on the PTFE surface. Adhesive-free adhesion was found to require a longer heat-assisted plasma treatment time than adhesive bonding in order to achieve a high adhesion strength such as 1 N/mm.

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Direct adhesion; epoxy/epoxides; fluoropolymers; heat-assisted plasma treatment; indirect adhesion; rubber

## Introduction

Polytetrafluoroethylene (PTFE) is a typical fluoropolymer consisting of only $CF_2$ chains. It has a number of advantages including high thermal resistance, low coefficient of friction, sliding property, high water and oil repellency, good antifouling characteristics, high weather resistance, and good electrical insulating behavior. Despite the numerous advantages of PTFE, its inability to readily bond with other types of materials can pose problems unless a special surface treatment is performed. A conventional method involving a corrosive solution containing sodium (Na) has been long used to modify the surface of PTFE [1–3]. Its adhesion property is drastically improved via immersion in a Na-containing corrosive solution. However, the corrosive

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solution poses several serious problems: it is hazardous to the environment and malodorous, and it tends to discolor and leave residual Na on the PTFE surface. A wet process non-containing Na was developed and the process using $KMnO_4/HNO_3$ improved adhesion property of PTFE by more than twice than untreated PTFE [4]. However, the adhesion strength of 1.1 MPa is not high and does not provide a practically sufficient mechanical strength. In addition, although the risk of $KMnO_4/HNO_3$ solution is lower than that of Na-containing solution, the risk of dry process is much lower than that of wet process using $KMnO_4/HNO_3$ solution. Therefore, a dry process that does not involve a corrosive solution has been needed for a long time.

Plasma treatment is a surface modification method based on a dry process and therefore this does not involve the use of a corrosive solution. Moreover, it has already been used to improve the adhesion strength of both adhesive bonding and adhesive-free adhesion. Practically, it has been used to enhance the adhesion properties of polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS), polyethylene terephthalate (PET), polyamide (PA), polyether ether ketone (PEEK), poly methyl methacrylate (PMMA), cyclo olefin polymer (COP), and liquid crystal polymer (LCP). The literature also includes numerous reports on the positive effects of plasma treatment on adhesive bonding in systems such as PE/epoxy adhesive (EP-adhesive), PP/EP-adhesive, PS/EP-adhesive, PET/EP-adhesive, PA/EP-adhesive, and PEEK/EP-adhesive [5–7] and on adhesive-free adhesion in systems such as PMMA/PMMA, COP/COP, PEEK/PEEK, and LCP/glass [8–11]. In recent years, there are reports on plasma and its applications for improving adhesion strength between different materials such as conductive paste/stretchable substrate (polydimethylsiloxane, polyimide) [12,13], carbon fiber reinforced plastics (CFRP) [14], and wood plastic composites [15]. Plasma-treated PTFE samples have been evaluated via several methods including water contact angle measurements, electron spin resonance (ESR) measurements, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and atomic force microscopy, and the changes in their surface conditions and morphology as a result of the treatment have been reported in detail [16–19]. However, data related to the adhesion strength of plasma-treated PTFE samples have not been reported. Although literature on the effect of plasma treatment on the adhesion properties of PTFE is sparse, the few existing reports indicate that this effect is weak [20–23]. That is, plasma treatment alone does not appear to improve the adhesion properties of PTFE. Therefore, surface modification involving a combination of plasma treatment and graft polymerization instead of adhesives was developed [24–27], resulting in high adhesion strengths between PTFE and other types of materials. Conversely, strong adhesive-free adhesion between PTFE and other types of materials has rarely been achieved using combinations of other than plasma treatment and graft polymerisation. In recent years, researchers have achieved extremely strong adhesion of PTFE/isobutylene–isoprene rubber (IIR) and PTFE/natural rubber without using either an adhesive or a grafting agent [28–30]. These authors reported that the effect of heating during plasma treatment improved the adhesion property of PTFE, and some of them named the method heat-assisted plasma treatment. However, these previous reports only discuss adhesive-free adhesion, not adhesive bonding. Thus, the adhesion properties of adhesive bonding and adhesive-free adhesion have not been yet compared. In the present study, we investigate the adhesion property of adhesive bonding for heat-assisted plasma-treated PTFE and compare the adhesion properties of adhesive bonding and adhesive-free adhesion. We then discuss the relation among adhesion strength, surface temperature during plasma treatment, plasma treatment time, radical density ratio, surface chemical composition, surface hardness, and surface morphology. It is known that a weak boundary layer (WBL) exists on polymer surface [31,32]. We conclude that a correlation exists between the plasma treatment time and the recovery of the WBL.

## Experimental

### Materials

Commercially available rolled PTFE sheet (NITOFLON® No. 900UL, Nitto Denko: Kita-ku, Osaka, Japan; thickness: 0.2 mm) was cut into specimens with dimensions of 45 mm × 70 mm. Unvulcanized IIR sheets of thickness ca. 2 mm were prepared according to the method described in a patent [33].

### Method

#### Plasma treatment

Before use, PTFE sheets were sequentially washed with acetone (99.5%, Kishida Chemical: Chuo-ku, Osaka, Japan) and pure water for 1 min each using an ultrasonic bath (USK-1R, AS- ONE: Nishi-ku, Osaka, Japan). The washed PTFE sheets were then dried using an air gun containing $N_2$ gas (99.99%, Iwatani Fine Gas: Amagasaki, Hyogo, Japan). The dried PTFE sheets were subsequently fixed onto a cylindrical rotation stage (W = 34 mm, ⌀40 mm) [29]. Finally, the PTFE sheets were plasma-treated using helium gas (99.99%, Iwatani Fine Gas) at atmospheric pressure in a custom-made chamber system (Meisyo Kiko: Tanba, Hyogo, Japan) [34] with a radio-frequency (RF) power source ($f$ = 13.56 MHz, KD-01, Noda RF Technologies: Suita, Osaka, Japan). The applied RF power density was fixed at 7.4 W/cm$^2$. The gap between the electrode and the surface of the PTFE sheet was 1 mm. Heating during plasma treatment was performed and controlled using a near-infrared-radiation line heater (KSC100-24/OU, K Sonic: Koshigaya, Saitama, Japan, W = 160 mm) with a switching power supply (PS5R-A24, Idec Izumi: Yodogawa-ku, Osaka, Japan). The surface temperature of the PTFE samples during plasma treatment was measured with a digital radiation thermometer system (FT-H40K and FT-50A, Keyence: Higashiyodogawa-ku, Osaka, Japan) [29]. Only the PTFE surface, not the unvulcanized rubber surface, was subjected to plasma treatment.

### *Adhesion strength tests*

To evaluate the adhesion property of adhesive bonding for plasma-treated PTFE samples, a two-component EP-adhesive (epoxy resin AV-138 and hardener HV-998, Nagase ChemteX: Nishi-ku, Osaka, Japan) was used. First, AV-138 and HV-998 were mixed at an AV-138/HV-998 mass ratio of 5/2. Second, the mixed adhesive was coated onto two stainless steel (SUS) square bars. The thickness of the adhesive layer was then controlled at 0.121 ± 0.005 mm using a variable-thickness applicator. Third, the plasma-treated PTFE was placed onto the adhesive layer. Fourth, the PTFE/EP-adhesive/SUS composite was heated at 80°C for 30 min using a hotplate (HHP-170D, AS-ONE) to harden any uncured EP-adhesive. Before measurement of the adhesion strength, the EP-adhesive attached to both sides of the PTFE sheet and SUS bars were removed using a cutter knife. The adhesion strength between the plasma-treated PTFE and the EP-adhesive was measured via 90° peel tests using a digital force gage (ZP-200N, Imada: Toyohashi, Aichi, Japan) and an electrically driven stand (MX-500N, Imada). The sweep rate was 60 mm/min. The adhesion strengths were calculated by dividing the average tensile strength by the width of the plasma-treated PTFE sheet (ca. 5 mm) on the EP-adhesive layer. Figure 1a shows a schematic of the adhesive bonding evaluation via 90° peel tests in the present study. To confirm the reproducibility, three samples for each plasma condition were prepared under each of the same conditions.

To evaluate the adhesion property of adhesive-free adhesion for the plasma-treated PTFE samples, unvulcanized IIR sheets were used. First, the plasma-treated PTFE samples were placed on the unvulcanized IIR sheets in a mold. Second, the PTFE/IIR assembly samples were compressed at approximately 10 MPa at 180°C for 10 min using a hot-pressing machine (AH-2003, AS-ONE). Here, no adhesives were used in the adhesion process. Third, the temperatures of the PTFE/IIR assembly samples were returned to room temperature. Fourth, the adhesion strengths of the PTFE/IIR assembly samples were measured via a T-peel test using a combination of a digital force gage (ZP-200N, Imada) and an electrically driven stand (MX-500N, Imada). The sweep rate was 60 mm/min. Finally, the adhesion strengths were calculated by dividing the average tensile strength by the width of the PTFE/IIR assembly sample (ca. 10 mm). Figure 1b shows a schematic of the adhesive-free adhesion evaluation setup used to conduct the T-peel tests in the present study. To confirm the reproducibility, three samples for each plasma condition were prepared under the same preparation conditions.

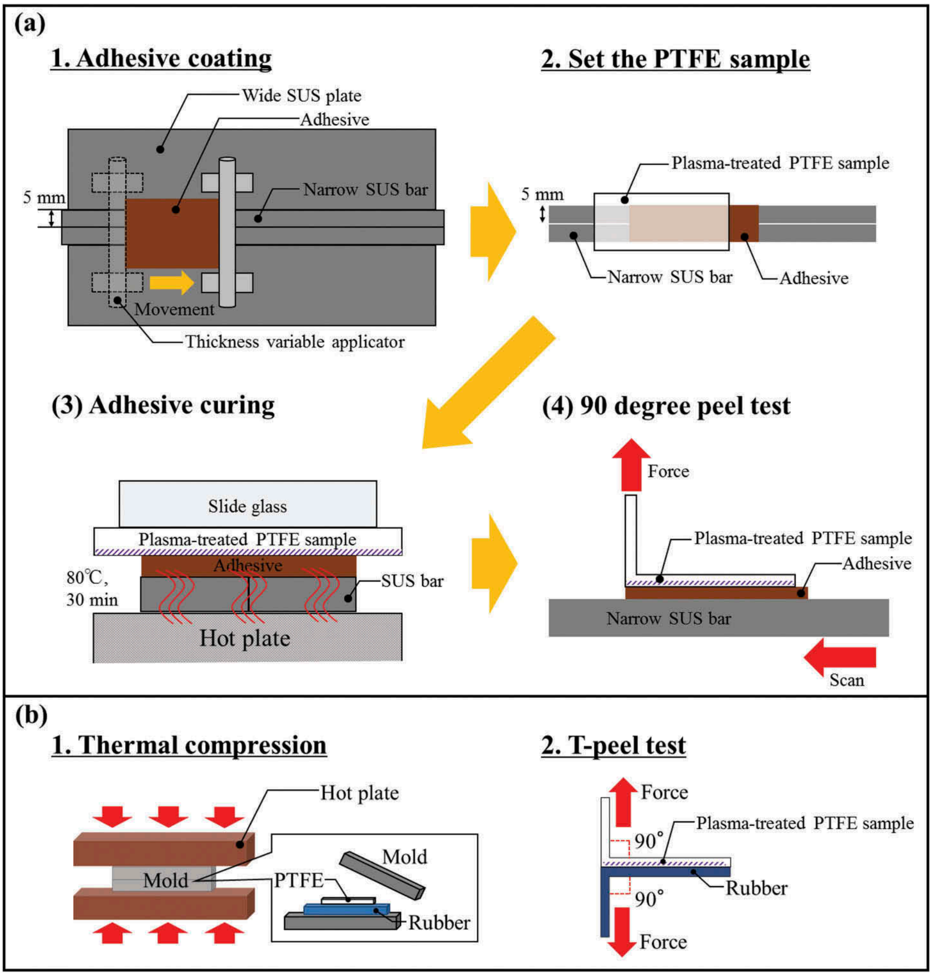

**Figure 1.** Schematic of adhesion property evaluation method. (a) adhesive bonding evaluation via the 90° peel test and (b) adhesive-free adhesion evaluation via the T-peel test. The shaded area indicates the plasma-treated side.

## *Electron spin resonance (ESR) measurements*

Peroxide radicals (C–O–O$^{\bullet}$) are known to form through the reaction between oxygen molecules in the atmosphere and the carbon radicals generated by the scission of C–F bonds upon plasma treatment [35]. To examine the radical density ratio of the plasma-treated PTFE, ESR measurements were conducted using an ESR spectrometer (JES-FA100x, JEOL: Akishima, Tokyo, Japan) operating at the X band frequency. The plasma-treated PTFE sample was cut into 3 mm × 30 mm × 0.2 mm specimens and inserted into a quartz glass cell (inner diameter 3 mm). The microwave power and the applied frequency were set to 10 mW and 10 GHz, respectively. ESR spectra were obtained at room temperature in the range from 329 to 341 mT. The fourth signal ($g_4$ = 1.981) of $Mn^{2+}$ in MgO was used as a reference. The radical density ratios were calculated by double integration of the intensity attributed to peroxide radicals. Each radical density ratio was normalized to the ESR spectrum of PTFE plasma-treated at 95°C for 600 s. Please note that ESR measurement is not sensitive to surface. In summary, we must pay attention to the ESR data after understanding it.

### X-ray photoelectron spectroscopy (XPS)

To examine changes in the chemical components on the surface of the plasma-treated PTFE samples and to clarify the location of the peeled interface in the samples of PTFE/EP-adhesive/SUS composite and the PTFE/IIR assembly, XPS measurements were conducted using a XPS spectrometer (Quantum 2000, Ulvac-Phi: Chigasaki, Kanagawa, Japan) equipped with an Al-*K*α source. The diameter of the X-ray irradiation area was ⌀100 μm, the take-off angle was 45°, the pass energy was 23.50 eV, and the step size was 0.05 eV. The C1s-XPS spectra were collected between 280 and 296 eV. The number of accumulated measurements was three. During the XPS measurement, a low-speed electron beam and an Ar ion beam were used to irradiate the measured samples to neutralize their surface charges. The binding energies of as-received and plasma-treated PTFE were referenced to the peak indexed to $-CF_2-$ at 292.5 and 291.8 eV, respectively [17,35–37].

### Surface energy

Contact angles of pure water and diiodomethane ($CH_2I_2$, 97.0%, Wako Pure Chemical Industries: Chuo-ku, Osaka, Japan) were measured on the plasma-treated PTFE samples using an automatic contact angle meter (DropMaster300, Kyowa Interface Science: Niiza, Saitama, Japan) with CCD camera. The droplet volume was 1 μL. Then total solid surface energies $\gamma_S{}^{total}$ were calculated using equations (1) and (2), derived by Owens and Wendt [38], where $\gamma_L{}^{total}$ is the total liquid surface energy, and $\theta$ is the experimental contact angle. Subscripts L and S denote liquid and solid surfaces, respectively. Superscripts d and h represent energies of the dispersion force and the hydrogen bonding force components, respectively. In equation (1), the $\gamma_L{}^d$ of 21.8 mN/m and $\gamma_L{}^h$ of 51.0 mN/m for water were used and the $\gamma_L{}^d$ of 49.5 mN/m and $\gamma_L{}^h$ of 1.3 mN/m for diiodomethane were used [38]; two equations that included two unknowns, $\gamma_S{}^d$ and $\gamma_S{}^h$, were derived. These unknowns were obtained by solving the simultaneous equations. The resulting values were used in equation (2) to obtain $\gamma_S{}^{total}$.

$$\gamma_L^{total}(1+cos\theta)=2(\gamma_S^d\gamma_L^d)^{1/2}+2(\gamma_S^h\gamma_L^h)^{1/2} \tag{1}$$

$$\gamma_S^{total} = \gamma_S{}^d + \gamma_S{}^h \quad (2)$$

### Surface topography

The surfaces of the plasma-treated PTFE samples were observed by SEM (JCM-6000, JEOL). Before observation, the plasma-treated PTFE samples were coated with gold thin layer using sputtering equipment (Smart Coat DII-29010SCTR, JEOL) to prevent electrification.

### Surface hardness tests

To examine the surface hardness of the plasma-treated PTFE samples, load–depth data were collected from 0 to 40 μN at 20 ms intervals using a nanoindenter (ENT-2100, Elionix: Hachioji, Tokyo, Japan). The indentation hardness was calculated by dividing the maximum load by the projected contact area. The surface hardness histograms were obtained by measuring the indentation hardness at 50 different points for each PTFE sample. The average surface hardness of the plasma-treated PTFE samples was then obtained as a geometric mean.

## Results and discussion

### Adhesion strength between plasma-treated PTFE and EP-adhesive

Figure 2 shows the adhesion strength of the plasma-treated PTFE/EP-adhesive/SUS composite samples with different plasma treatment times and with or without heating. For the as-received PTFE, the PTFE/EP-adhesive adhesion strength was 0 N/mm. When the PTFE was plasma-treated at 95°C

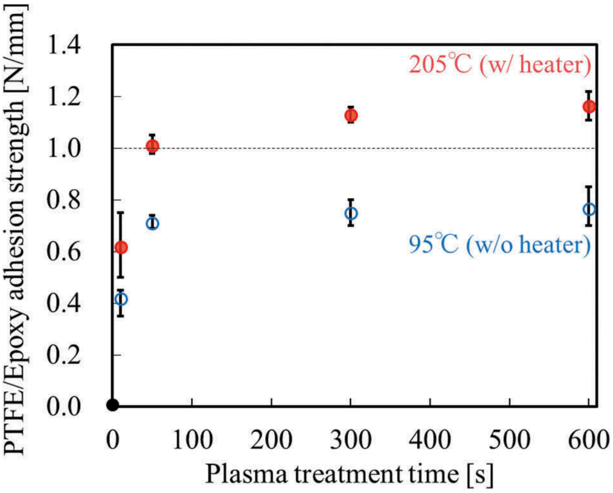

**Figure 2.** Adhesion strength of plasma-treated PTFE/EP-adhesive/SUS composite samples with different plasma treatment times with or without heating ($n$ = 3).

without using a heater, the adhesion strengths did not reach 1 N/mm regardless of the duration of the plasma treatment time. When the PTFE was plasma-treated at 205°C using a heater for more than 50 s, its adhesion strength became greater than 1 N/mm. In addition, when the PTFE was plasma-treated at 205°C for only 20 s, its adhesion strength was the same as that of PTFE plasma-treated at 95°C for more than 50 s (not shown here). These results indicate that heating during plasma treatment effectively both improved the adhesion property of adhesive bonding of the PTFE and increased the speed of surface modification.

## Adhesion strength between plasma-treated PTFE and IIR

Figure 3 shows the adhesion strength of the plasma-treated PTFE/IIR assembly samples with different plasma treatment times and with or without heating. For the as-received PTFE, the PTFE/IIR adhesion strength was 0 N/mm. When PTFE was plasma-treated at 95°C without using a heater, its PTFE/IIR adhesion strength was < 0.5 N/mm, regardless of the duration of plasma treatment time. When PTFE was plasma-treated at 205°C using a heater, its PTFE/IIR adhesion strength reached 2 N/mm at a plasma treatment time greater than 300 s; cohesion failure of the IIR then occurred.

For adhesive bonding, 1 N/mm of PTFE/EP-adhesive/SUS composite was achieved when the PTFE was plasma-treated for only 50 s (Figure 2). In contrast, for adhesive-free adhesion, a PTFE/IIR adhesion strength of 1 N/mm was not achieved at a treatment time of 50 s, however, a PTFE/IIR adhesion strength of > 2 N/mm was finally achieved at a treatment time of 300 s (Figure 3). These results indicate that adhesive-free adhesion requires a

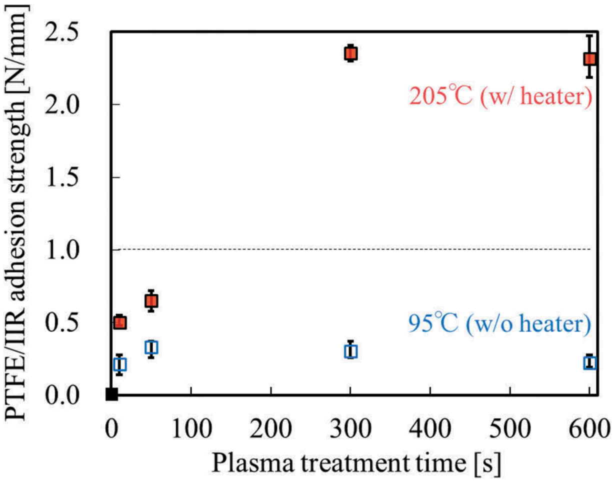

**Figure 3.** Adhesion strength of plasma-treated PTFE/IIR assembly samples with different plasma treatment times with or without heating ($n$ = 3).

longer plasma treatment time than adhesive bonding in order to achieve a high adhesion strength (> 1 N/mm) of PTFE.

## Heating effect on the chemical and physical properties of PTFE

To clarify the difference in plasma treatment times required for high adhesion strength between adhesive bonding and adhesive-free adhesion, SEM observations and measurements using ESR, XPS, and surface hardness tests were conducted.

Figure 4a and 4b shows the eight representative ESR spectra for the plasma-treated PTFE samples with different plasma treatment times and with or without heating. The ESR spectra of the as-received and just-heated PTFE samples (non-plasma-treated and only heated at 205°C for 600 s) showed the peaks indexed to $Mn^{2+}$ markers at ca. 331 and 340 mT but no peaks indexed to the peroxide radical (C–O–O$^\bullet$). All the ESR spectra of the plasma-treated PTFE samples showed broad peaks indexed to the peroxide radical (C–O–O$^\bullet$) between 332 and 337 mT. The shapes of all the ESR spectra with peaks indexed to the peroxide radical were asymmetric. These results

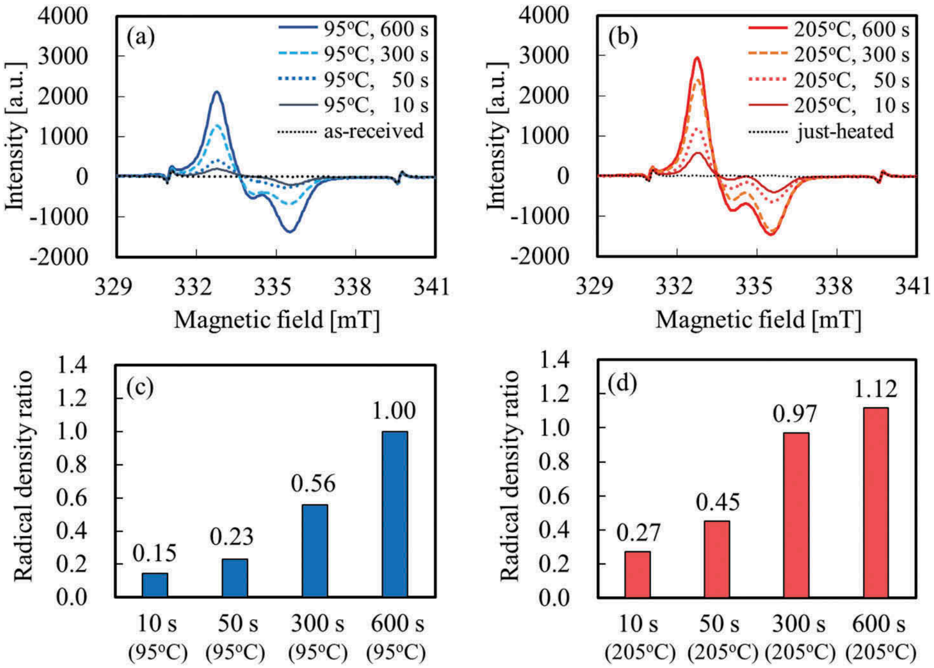

**Figure 4.** ESR results for plasma-treated PTFE samples. (a) ESR spectra of plasma-treated PTFE samples without heating, (b) ESR spectra of plasma-treated PTFE samples with heating, (c) radical density ratio of plasma-treated PTFE samples without heating, and (d) radical density ratio of plasma-treated PTFE samples with heating.

indicate that the peroxide radicals in this study contained more mid-chain-type ($-CF_2CFOO^{\bullet}CF_2-$) than end-chain-type ($-CF_2CF_2CF_2OO^{\bullet}$) [35].

Figure 4c and 4d shows the eight representative radical density ratios of the plasma-treated PTFE samples with different plasma treatment times and with or without heating. The radical density ratios increased with increasing plasma treatment time regardless of heating during plasma treatment. In case where the plasma treatment time was the same, all the radical density ratios increased upon heating during plasma treatment. The radical density ratio of PTFE plasma-treated at 95°C for 600 s (1.00) was higher than that of PTFE plasma-treated at 205°C for 50 s (0.45). In contrast, the adhesion strengths of adhesive bonding and adhesive-free adhesion for PTFE plasma-treated at 95°C for 600 s (0.77 N/mm in Figures 2 and 0.22 N/mm in Figure 3, respectively) were lower than those of adhesive bonding and adhesive-free adhesion for PTFE plasma-treated at 205°C for 50 s (1.01 N/mm in Figures 2 and 0.65 N/mm in Figure 3, respectively). In summary, the adhesion property and the radical density ratio exhibited poor correlation in this study. The difference in adhesion strengths cannot be explained on the basis of the radical density ratio. Thus, factors other than the radical density ratio must be responsible for the improvement in the adhesion strength. Here, remember that the depth range of ESR measurement is a millimeter order, not sensitive to surface. Although we assumed that peroxide radicals generated and existed near to the plasma-treated PTFE surface, it is not known whether the radicals actually generated near to the surface and remained or not. Therefore, next we performed XPS measurement because the depth range of XPS measurement is a nanometer order and sensitive to surface.

Figure 5 shows the four representative C1s-XPS spectra for the plasma-treated PTFE samples with different plasma treatment times and with or without heating. For comparison, the XPS spectrum of the as-received PTFE was obtained (Figure 5a). The intensity of the peak indexed to fluorine-containing functional groups (i.e., $CF_3$, $CF_2$, and C–F) at ca. 294–290 eV decreased upon plasma treatment compared with the intensity of the corresponding peak in the spectrum of the as-received PTFE. This result indicates that C–F bond scissions occurred on the PTFE surface upon plasma treatment. In addition, the peaks indexed to oxygen-containing functional groups (O–C=O, C=O, and C–O) and carbon-containing functional groups (C–C, C–H, and C=C) appeared at ca. 289–286 eV [36,37] and ca.286–284 eV [39], respectively. These results indicate that a part of the carbon radicals reacted with other carbon radicals during plasma treatment, followed by C–C cross-linking [31]; moreover, the remaining carbon radicals reacted with oxygen and/or moisture in the air, generating oxygen-containing functional groups generated. These results were well consistent with a previous report [29].

For further analysis, the peaks in the C1s-XPS spectra were deconvoluted. Table 1 shows the ratios of fluorine, oxygen, and carbon groups for the four

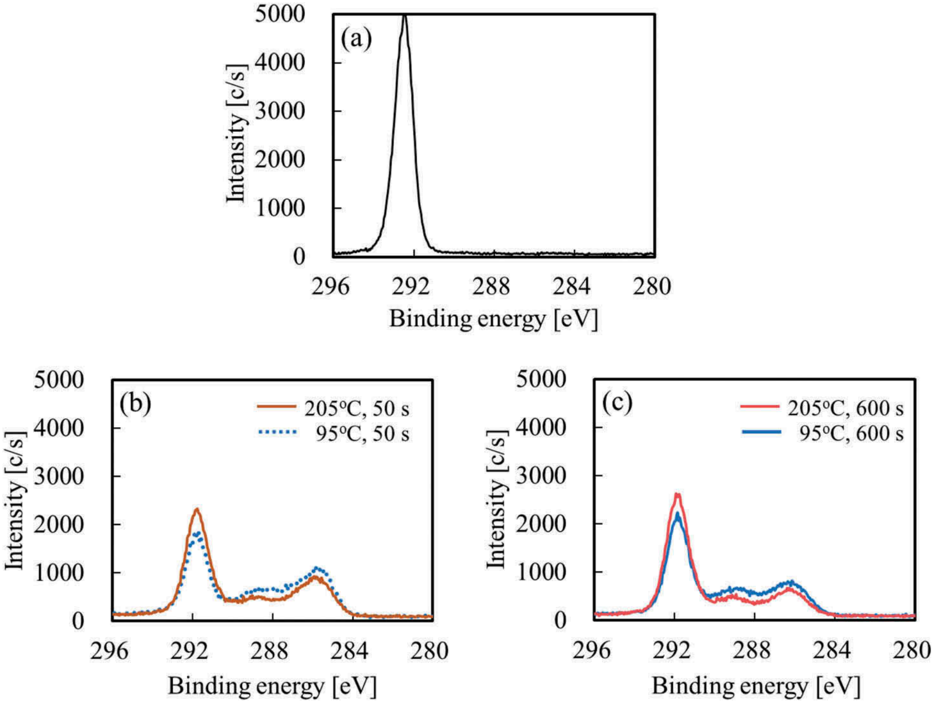

**Figure 5.** Representative four types of C1s-XPS spectra of plasma-treated PTFE samples with different plasma treatment times and with or without heating. (a) as-received, (b) short plasma treatment time: 50 s, and (c) long plasma treatment time: 600 s.

**Table 1.** Surface chemical composition, calculated from the C1s-XPS spectra in Figure 5, radical density ratio, and adhesion properties.

| Sample name | As-received | 95°C_50s | 205°C_50s | 95°C_600s | 205°C_600s |
|---|---|---|---|---|---|
| fluorine group [%] | 100 | 47 | 59 | 58 | 70 |
| Oxygen group [%] | 0 | 32 | 28 | 35 | 25 |
| Carbon group [%] | 0 | 21 | 13 | 8 | 5 |
| Radical density ratio | 0.00 | 0.23 | 0.45 | 1.00 | 1.12 |
| Adhesion to EP-adhesive | × | Δ | ◎ | Δ | ◎ |
| Adhesion to IIR | × | × | Δ | × | ◎ |

* ×: ≤ 0.5 N/mm; Δ: 0.5–0.8 N/mm; ○: 0.8–1.0 N/mm; ◎: ≥ 1.0 N/mm.

representative plasma-treated PTFE samples with different plasma treatment times and with or without heating; these ratios were calculated from the resolved peaks in the C1s-XPS spectra of Figure 5. For comparison between ESR and XPS results, the radical density ratios of peroxide radicals were added to Table 1. Although the radical density ratios increased with increasing the surface temperature, the oxygen group ratio decreased with increasing the surface temperature. These results indicated that peroxide radicals exist not only near to the surface but also in the bulk. The correlation between thickness of plasma-modified layer and adhesion strength is not clear and the detail should be discussed in the future. For comparison between adhesion property and XPS results, the results of adhesion strength were also added to Table 1. The fluorine group ratio of plasma-treated PTFE at 205°C for 50 s (59%) was higher than that of plasma-treated PTFE at 95°C for 50 s (47%), and the fluorine group ratio of plasma-treated PTFE at 205°C for 600 s (70%) was also higher than that of plasma-treated PTFE at 95°C for 600 s (58%). These results indicate that heating during plasma treatment promotes etching on the PTFE surface. In contrast, the oxygen group ratio of PTFE plasma-treated at 205°C for 50 s (28%) was lower than that of PTFE plasma-treated at 95°C for 50 s (32%), and the oxygen group ratio of PTFE plasma-treated at 205°C for 600 s (25%) was also lower than that of PTFE plasma-treated at 95°C for 600 s (35%). The adhesion property of PTFE plasma-treated at 205°C for 50 s was higher than that of PTFE plasma-treated at 95°C for 50 s, and the adhesion property of PTFE plasma-treated at 205°C for 600 s was also higher than that of PTFE plasma-treated at 95°C for 600 s (Figure 2, Figure 3, and Table 1), although oxygen-containing functional groups are generally known to enhance adhesion [10,11,27,40]. From this viewpoint of surface chemical composition, the oxygen group ratio of 25% was sufficient to achieve for both strong adhesive bonding and adhesive-free adhesion. That is, the low improvement in the adhesion property of PTFE plasma-treated without heating cannot be explained by surface chemical composition.

Table 2 shows the contact angles and surface energies for the four representative plasma-treated PTFE samples with different plasma treatment times and with or without heating. All the plasma-treated PTFE samples indicated a higher $\gamma_S^{total}$ than as-received PTFE (15.4 mN/m). Furthermore, the $\gamma_S^{total}$ of plasma-treated PTFE at 205°C for 50 s (25.3 mN/m) was lower than that of plasma-treated PTFE at 95°C for 50 s (57.6 mN/m), and the $\gamma_S^{total}$ of plasma-treated PTFE at 205°C for 600 s (20.8 mN/m) was also lower than that of plasma-treated PTFE at 95°C for 600 s (42.8 mN/m). These results indicate that heating during plasma treatment decreased the $\gamma_S^{total}$. Although it is generally known that increase in $\gamma_S^{total}$ contributes to increase in adhesion property, reverse behaviour was observed in the present study.

**Table 2.** Contact angles and surface energies calculated from two equations (1) and (2), derived by Owens and Wendt [38].

| Sample name | As-received | 95°C_50s | 205°C_50s | 95°C_600s | 205°C_600s |
|---|---|---|---|---|---|
| Contact angle of water [deg.] | 115.2±1.0 | 43.3±1.9 | 109.0±3.5 | 64.8±2.5 | 103.7±1.6 |
| Contact angle of diiodomethane [deg.] | 84.3±1.8 | 39.8±1.4 | 66.4±4.3 | 49.4±2.7 | 73.8±1.3 |
| Surface energy $\gamma_s^{d}$ [mN/m] | 15.3 | 30.7 | 25.3 | 28.6 | 19.9 |
| Surface energy $\gamma_s^{h}$ [mN/m] | 0.1 | 26.9 | 0.0 | 14.2 | 1.0 |
| Total surface energy $\gamma_s^{total}$ [mN/m] | **15.4** | **57.6** | **25.3** | **42.8** | **20.8** |

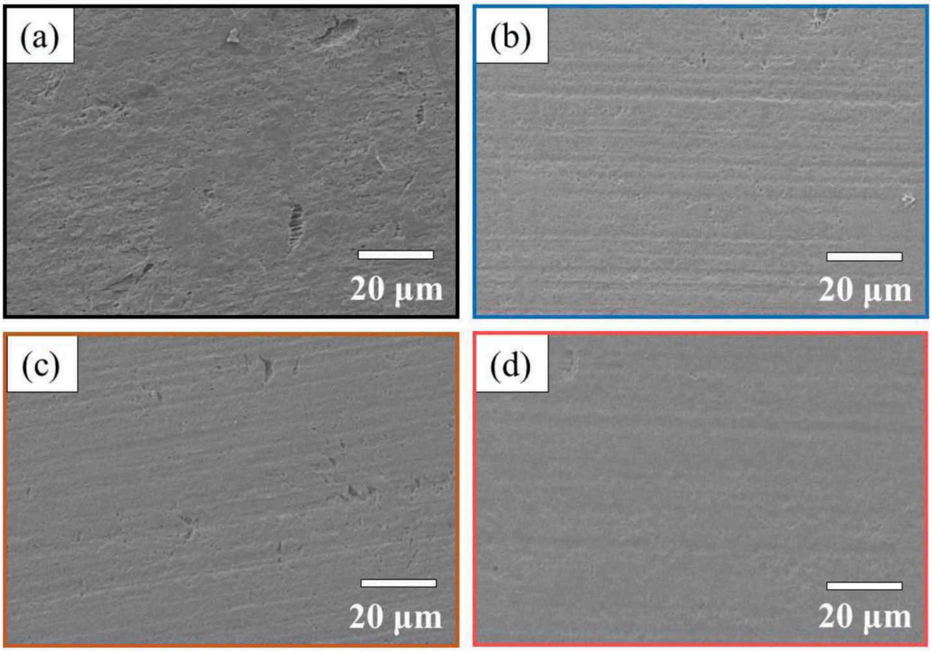

**Figure 6.** Representative four types of SEM images of PTFE surface before and after plasma treatment. (a) as-received, (b) plasma-treated at 95°C for 600 s, (c) plasma-treated at 205°C for 50 s, and (d) plasma-treated at 205°C for 600 s.

The adhesion property of plasma-treated PTFE could not be determined based on the surface chemical composition, particularly the oxygen group ratio, and solid surface energy. In other words, other factors must be considered for improving the adhesion strength. Next, the surface morphology of the PTFE samples was observed using SEM. Figure 6 shows SEM images of four representative PTFE surfaces before and after plasma treatment. Several cutting scratches and pits were observed on the surface of the as-received PTFE, which means that the PTFE originally had a WBL. The number of pits decreased, but scratches remained on the PTFE plasma-treated at 95°C for 600 s and the PTFE plasma-treated at 205°C for 50 s, which means that the WBL remained on the PTFE surface. Almost no pits and scratches were observed on the PTFE plasma-treated at 205°C for 600 s. In the case of long plasma treatment times such as 600 s, the WBL of PTFE would be sufficiently recovered and/or removed, that is to say, etching of WBL and/or formation of C–C crosslinking would occur to prevent peeling in the WBL. In addition, the PTFE plasma-treated at 205°C had the lowest surface roughness but the highest adhesion property, which indicated that a WBL recovery was more effective for improvement in adhesion property of PTFE than micro-level surface roughness.

Figure 7 shows surface hardness histograms of four representative PTFE surfaces before and after plasma treatment. The surface hardness of the PTFE plasma-treated at 95°C for 600 s (129 MPa) was slightly higher than that of the

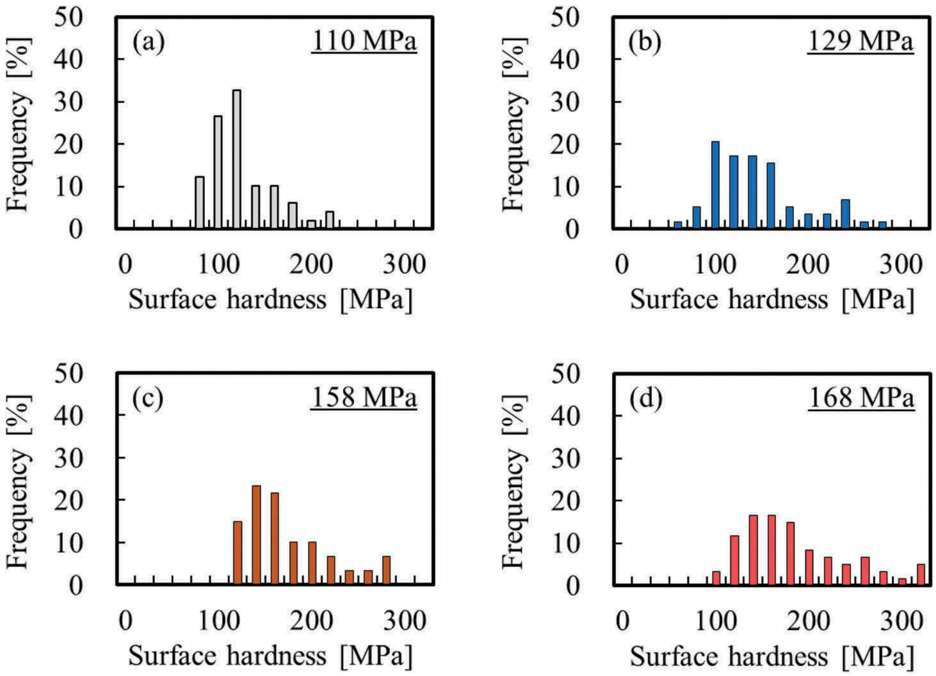

**Figure 7.** Representative four types of surface hardness histograms of PTFE samples before and after plasma treatment. (a) as-received, (b) plasma-treated at 95°C for 600 s, (c) plasma-treated at 205°C for 50 s, and (d) plasma-treated at 205°C for 600 s.

as-received PTFE (110 MPa). In contrast, the surface hardness of the PTFE plasma-treated at 205°C for 50 s (158 MPa) was higher than that of the PTFE plasma-treated at 95°C for 600 s (129 MPa). This result indicates that the surface hardness drastically increased upon heating during plasma treatment even though the plasma treatment time was short. In addition, the surface hardness of the PTFE plasma-treated at 205°C for 600 s (168 MPa) was higher than that of the PTFE plasma-treated at 205°C for 50 s (158 MPa). This result indicates that the surface hardness increased with increasing plasma treatment time. In the SEM images of Figure 6, pits and scratches also decreased with increasing plasma treatment time, which meant that the WBL recovery was advanced with increasing plasma treatment time. The SEM observations are well consistent with the results related to surface hardness. Moreover, the adhesion property of the plasma-treated PTFE increased with increasing surface hardness. In summary, an increase in surface hardness would also mean a recovery of the WBL on the PTFE surface and consequently the adhesion property of the plasma-treated PTFE was improved.

Figure 8 shows the XPS spectra of the peeled surfaces of heat-assisted plasma-treated PTFE/EP-adhesive/SUS composite samples with different plasma treatment times. When the PTFE was plasma-treated at 205°C for 50 s, $CF_2$ and F derived from PTFE were detected, whereas C–O and C–H (C–C) derived from the

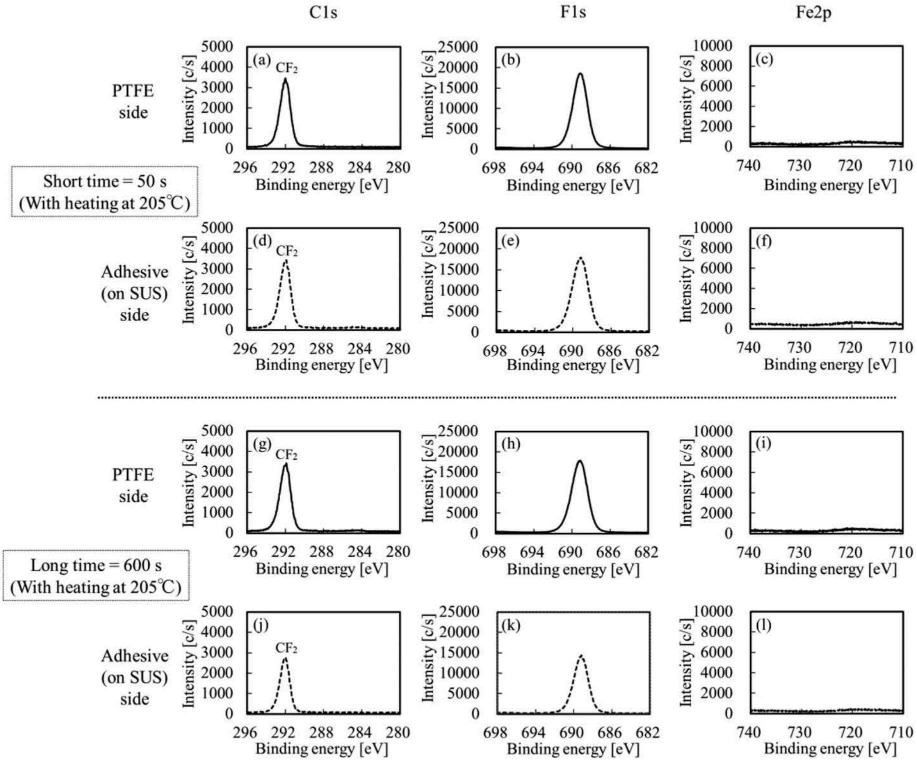

**Figure 8.** XPS spectra of the peeled surfaces of heat-assisted plasma-treated PTFE/EP-adhesive/SUS composite samples with different plasma treatment times. (a) C1s-XPS spectrum of the PTFE side at short time: 50 s, (b) F1s-XPS spectrum of the PTFE side at short time: 50 s, (c) Si2p-XPS spectrum of the PTFE side at short time: 50 s, (d) C1s-XPS spectrum of the EP-adhesive side at short time: 50 s, (e) F1s-XPS spectrum of the EP-adhesive side at short time: 50 s, (f) Si2p-XPS spectrum of the EP-adhesive side at short time: 50 s, (g) C1s-XPS spectrum of the PTFE side at long time: 600 s, (h) F1s-XPS spectrum of PTFE the side at long time: 600 s, (i) Si2p-XPS spectrum of the PTFE side at long time: 600 s, (j) C1s-XPS spectrum of the EP-adhesive side at long time: 600 s, (k) F1s-XPS spectrum of the EP-adhesive side at long time: 600 s, and (l) Si2p-XPS spectrum of the EP-adhesive side at long time: 600 s.

EP-adhesive and Fe derived from the SUS were not detected at all on the peeled surface of the PTFE side (Figure 8a–8c). Similar results were obtained for the peeled surface of the adhesive side (Figure 8d–8f). These results indicates that peeling occurred in the PTFE bulk layer but neither in the EP-adhesive nor at the interface between the EP-adhesive and the SUS, that is to say, cohesion failure of bulk PTFE occurred for the PTFE plasma-treated at 205°C for 50 s. When the PTFE was plasma-treated at 205°C for 600 s, the XPS spectra of the peeled surfaces (Figure 8g–8l) were almost the same as those of the peeled surfaces of both the PTFE side and the adhesive side for the PTFE plasma-treated at 205°C for 50 s (Figure 8a–8f). These results indicate that the peeling also occurred in the PTFE bulk layer but not in the EP-adhesive, that is to say, cohesion failure of bulk PTFE occurred for the PTFE plasma-treated at 205°C for 600 s.

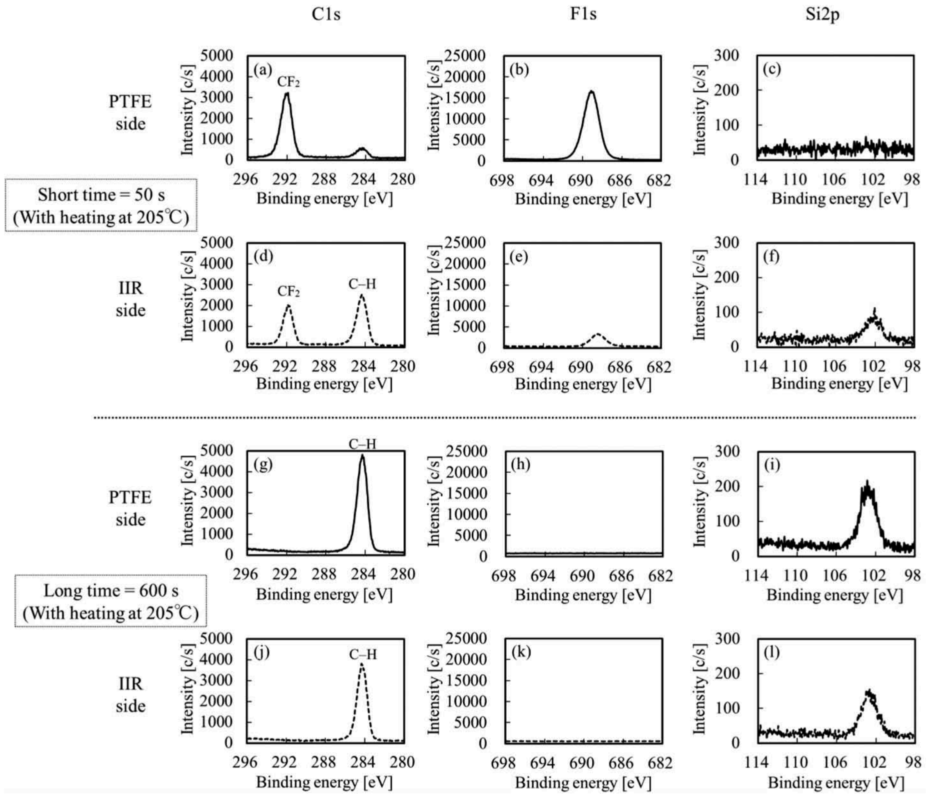

**Figure 9.** XPS spectra of the peeled surfaces of heat-assisted plasma-treated PTFE/IIR assembly samples with different plasma treatment times. (a) C1s-XPS spectrum of the PTFE side at short time: 50 s, (b) F1s-XPS spectrum of the PTFE side at short time: 50 s, (c) Si2p-XPS spectrum of the PTFE side at short time: 50 s, (d) C1s-XPS spectrum of the IIR side at short time: 50 s, (e) F1s-XPS spectrum of the IIR side at short time: 50 s, (f) Si2p-XPS spectrum of the IIR side at short time: 50 s, (g) C1s-XPS spectrum of the PTFE side at long time: 600 s, (h) F1s-XPS spectrum of the PTFE side at long time: 600 s, (i) Si2p-XPS spectrum of the PTFE side at long time: 600 s, (j) C1s-XPS spectrum of the IIR side at long time: 600 s, (k) F1s-XPS spectrum of the IIR side at long time: 600 s, and (l) Si2p-XPS spectrum of the IIR side at long time: 600 s.

Figure 9 shows the XPS spectra of the peeled surfaces of heat-assisted plasma-treated PTFE/IIR samples with different plasma treatment times. On the peeled surface of the PTFE side of the sample plasma-treated at 205°C for 50 s, $CF_2$ and F derived from PTFE and a small amount of C–H (C–C) derived from IIR were detected, whereas Si derived from IIR was not detected (Figure 9a–9c). On the peeled surface of the IIR side of the same sample, C–H (C–C) and Si derived from IIR were detected in addition to $CF_2$ and F derived from PTFE were also detected (Figure 9d–9f). These results indicate that the peeling occurred mostly in the WBL of PTFE and partly at the interface of PTFE and IIR but not at the plasma-modified PTFE surface, that is to say, a mixture of cohesion failure of PTFE in the WBL and interfacial peeling occurred for the PTFE plasma-treated at 205°C for 50 s.

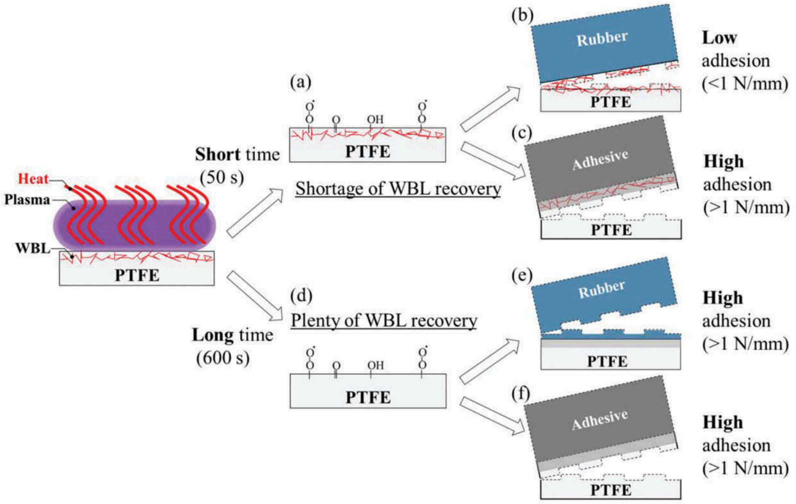

**Figure 10.** Model showing the adhesion improvement for the plasma-treated PTFE. (a) short plasma treatment time, (b) short plasma treatment time for adhesive-free adhesion, (c) short plasma treatment time for adhesive bonding, (d) long plasma treatment time, (e) long plasma treatment time for adhesive-free adhesion, and (f) long plasma treatment time for adhesive bonding.

When the PTFE was plasma-treated at 205°C for 600 s, $CF_2$ and F derived from PTFE were not detected at all, whereas C–H (C–C) and Si derived from IIR were detected on the peeled surface of the PTFE side (Figure 9g–9i). Similar results were obtained for the peeled surface of the IIR side (Figure 9j–9l). These results indicate that peeling occurred in the IIR bulk layer. That is, cohesion failure of rubber occurred for the PTFE plasma-treated at 205°C for 600 s.

This dramatic difference between adhesive bonding and adhesive-free adhesion is attributable to the existence of the WBL and to the fluidity of the adherent. Figure 10 presents a model showing the difference in adhesion improvements for the heat-assisted plasma-treated PTFE. In the case of a short plasma treatment time such as 50 s, a shortage of WBL recovery would occur (Figure 10a). For adhesive-free adhesion, unvulcanized rubber would not soak into the WBL because of its low fluidity. Therefore, low adhesion strength would be obtained (Figure 10b). In contrast, for adhesive bonding, the adhesive would soak into the WBL and then harden itself with the WBL. Therefore, high adhesion strength would be obtained despite a shortage of WBL recovery (Figure 10c). In the case of a long plasma treatment time such as 600 s, the WBL of PTFE would be sufficiently recovered to prevent peeling in the WBL (Figure 10d). Therefore, the adhesion strengths of both adhesive-free adhesion and adhesive bonding would become high (Figure 10e and 10f).

## Conclusion

We prepared plasma-treated PTFE samples with different plasma treatment times and with or without heating to compare the adhesion properties of adhesive bonding and adhesive-free adhesion of PTFE. In the case of short heat-assisted plasma treatment times such as 50 s, WBL recovery was insufficient. Therefore, the adhesion strength of PTFE/IIR was much lower than 1 N/mm because of peeling of the remaining WBL of PTFE. In contrast, the adhesion strength of PTFE/EP-adhesive was greater than 1 N/mm despite of a shortage of WBL recovery because the EP-adhesive could harden itself with the WBL. In the case of long heat-assisted plasma treatment times such as 600 s, plenty of WBL recovery occurred. Therefore, the adhesion strengths of both PTFE/IIR and PTFE/EP-adhesive were greater than 1 N/mm. In summary, we found that heat-assisted plasma treatment effectively improved the adhesion properties of both adhesive bonding and adhesive-free adhesion of PTFE, whereas adhesive-free adhesion required a longer heat-assisted plasma treatment time than adhesive bonding for WBL recovery. In addition, we concluded that heating during plasma treatment affected the ratio of two essential reactions of etching and formation of functional groups from the results of XPS, SEM, and surface hardness. It was previously reported that two essential reactions of etching and formation of functional groups occurred on polymer surfaces when they are exposed to plasma [41]. From the XPS results, heating during plasma treatment decreased the ratio of oxygen groups and increased the ratio of fluorine groups, which indicated that heating during plasma treatment decreased the ratio of formation of functional groups and increased the ratio of etching. From the results of SEM observation and surface hardness measurement, it was clear that heating during plasma treatment increased the etching rate. In summary, heating during plasma treatment promoted a reaction of etching, and moreover plenty of formation of functional groups occurred for high adhesion although the increase ratio of etching was higher than that of formation of functional groups. We expect these results to provide guidance for achieving strong adhesive-free adhesion of PTFE.

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## Notes on contributor

Yuji Ohkubo, K. Endo, and K. Yamamura supervised the work. Y. Ohkubo fabricated the polytetrafluoroethylene samples. M. Shibahara and A. Nagatani fabricated the isobutylene–isoprene rubber samples. Y. Ohkubo performed the experiments. M. Shibahara, A. Nagatani,

K. Honda, K. Endo, and K. Yamamura commented on the measurements. All authors contributed to scientific discussions and to manuscript preparation. Y. Ohkubo wrote the manuscript.

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