



Title	Effect of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated polytetrafluoroethylene (PTFE)
Author(s)	Ohkubo, Yuji; Shibahara, Masafumi; Ishihara, Kento et al.
Citation	Journal of Adhesion. 2018, 95(3), p. 242-257
Version Type	VoR
URL	https://hdl.handle.net/11094/84519
rights	© 2018 The Author(s). Published by Taylor & Francis. This is an Open Access article. Non-commercial re-use, distribution, and reproduction in any medium, provided the original work is properly attributed, cited, and is not altered, transformed, or built upon in any way, is permitted. The moral rights of the named author(s) have been asserted.
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka



Effect of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated polytetrafluoroethylene (PTFE)

Yuji Ohkubo, Masafumi Shibahara, Kento Ishihara, Asahiro Nagatani, Koji Honda, Katsuyoshi Endo & Kazuya Yamamura

To cite this article: Yuji Ohkubo, Masafumi Shibahara, Kento Ishihara, Asahiro Nagatani, Koji Honda, Katsuyoshi Endo & Kazuya Yamamura (2019) Effect of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated polytetrafluoroethylene (PTFE), The Journal of Adhesion, 95:3, 242-257, DOI: [10.1080/00218464.2018.1428095](https://doi.org/10.1080/00218464.2018.1428095)

To link to this article: <https://doi.org/10.1080/00218464.2018.1428095>



© 2018 The Author(s). Published by Taylor & Francis.



Published online: 14 Feb 2018.



Submit your article to this journal [↗](#)



Article views: 466



View Crossmark data [↗](#)



Citing articles: 1 View citing articles [↗](#)



Effect of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated polytetrafluoroethylene (PTFE)

Yuji Ohkubo ^a, Masafumi Shibahara^b, Kento Ishihara^a, Asahiro Nagatani^b, Koji Honda^c, Katsuyoshi Endo^a, and Kazuya Yamamura^a

^aGraduate School of Engineering, Osaka University, Suita, Japan; ^bHyogo Prefectural Institute of Technology, Kobe, Japan; ^cTechnical Support Center for Leather Industries, Hyogo Prefectural Institute of Technology, Hyogo, Japan

ABSTRACT

Although heat-assisted plasma treatment enables drastic improvement of the adhesion property of polytetrafluoroethylene (PTFE), plasma-treated PTFE does not strongly adhere to any adherend. To clarify which rubber compounding agents positively affect the adhesion strength of a plasma-treated PTFE/rubber assembly, six types of unvulcanised rubbers were prepared and thermally compressed to a plasma-treated PTFE sheet. Thus, it was found that SiO₂ addition to rubber drastically increased the adhesion strength of a plasma-treated PTFE/rubber assembly and cohesion failure of rubber occurred with large fractions of SiO₂ although no adhesives were used. To confirm the reaction between plasma-treated PTFE and SiO₂ powder, X-ray photoelectron spectroscopy (XPS) measurements were performed for the thermally compressed SiO₂/PTFE assembly after repeated washing. The XPS results indicated that hydrophilic SiO₂ powder strongly adhered to the plasma-treated PTFE, whereas hydrophobic SiO₂ powder did not adhere to the PTFE. In this paper, a model was proposed for a possible mechanism of strong adhesion of a PTFE/rubber assembly through both hydrogen and covalent bonds between silanol groups of the SiO₂ powder surface in the rubber and hydroxyl or carboxyl groups on the plasma-treated PTFE.

ARTICLE HISTORY

Received 2 November 2017;
Accepted 11 January 2018

KEYWORDS

Adhesive-free adhesion; fluoropolymers; rubber compounding agent; silica; surface treatment by exited gases; X-ray photoelectron spectroscopy

Introduction

Rubber has elasticity but poor chemical resistance and sliding properties. In contrast, polytetrafluoroethylene (PTFE), which is a fluoropolymer, has high chemical resistance and good sliding properties but no elasticity. Combining rubber and PTFE can compensate for the disadvantages of

CONTACT Yuji Ohkubo okubo@upst.eng.osaka-u.ac.jp Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan.

Y. Ohkubo, K. Endo, and K. Yamamura supervised the work. K. Ishihara and Y. Ohkubo fabricated the PTFE samples. M. Shibahara and A. Nagatani fabricated the IIR samples. M. Shibahara, K. Honda, and Y. Ohkubo performed the experiments. K. Yamamura and K. Endo give comments to the measurements. All authors contributed to the scientific discussion and the manuscript preparation. Y. Ohkubo wrote the manuscript.

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gadh.

© 2018 The Author(s). Published by Taylor & Francis.

This is an Open Access article. Non-commercial re-use, distribution, and reproduction in any medium, provided the original work is properly attributed, cited, and is not altered, transformed, or built upon in any way, is permitted. The moral rights of the named author(s) have been asserted.

both materials. However, PTFE does not easily adhere to other types of materials. PTFE not only has an extremely low surface energy, in common with fluoropolymers, but also has a weak boundary layer (WBL).^[1,2] Therefore, it is essential not only to generate oxygen-containing radicals and functional groups on PTFE surfaces but also to remove and/or recover the WBL of PTFE surface to improve its adhesion property. To generate oxygen-containing radicals and functional groups and remove and/or recover the WBL, corrosive solutions such as sodium–naphthalene and sodium–ammonium complex solutions have been used as conventional methods.^[3,4] As a result, the adhesion properties of PTFE drastically improved. However, corrosive solutions have significant disadvantages: a negative impact on humans and the environment, strong odours, and sodium residues on PTFE. An alternative method that does not require the corrosive solutions has, therefore, long been needed. Although many researchers attempted to develop an alternative method via surface treatments involving dry processes such as ion and plasma irradiation, the realisation of good adhesion properties of PTFE (over 1 N/mm) has been difficult.^[5–9] Therefore, several combinations of surface treatments such as plasma irradiation and surface graft polymerisation were developed.^[4,10–12] In addition, in recent years, good adhesion properties of PTFE were realised without graft polymerisation under special conditions of ion or plasma irradiation by Yumoto's^[13] and Ohkubo's groups.^[14,15] Yumoto's group reported that the adhesion strength between ion-irradiated PTFE and polypropylene tape containing glass fibre through an epoxy adhesive drastically increased to 1.5 N/mm upon N₂ ion irradiation under a high acceleration voltage. Ohkubo's group reported that the adhesion strength between plasma-treated PTFE and isobutylene–isoprene rubber (IIR) drastically increased to over 2.0 N/mm upon helium (He) heat-assisted plasma treatment at above 200°C. In the report, cohesion failure of IIR occurred in the middle of T-peel test despite the absence of adhesives and graft polymerisation agents. Although Ohkubo *et al.* studied a modified PTFE surface in detail by electron spin resonance (ESR) measurement, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy, atomic force microscopy, nanoindentation, and contact angle measurement and achieved extremely strong adhesion between the plasma-treated PTFE and other materials, the rubber surface was barely studied. Thus, the mechanism of strong adhesion is unclear. Although there are several reports on improved adhesion strength between rubber and metal without using adhesives^[16–19], there are few reports on the improvement of the adhesion strength between rubber and plasma-treated fluoropolymers. In this study, we prepared six types of rubbers to clarify which components in rubber affect the adhesion strength of a plasma-treated PTFE/rubber assembly. In addition, a direct

adhesion test of the rubber compounding agent, which induces strong adhesion, with the plasma-treated PTFE was performed.

Experimental

Materials

Commercially available PTFE sheet (NITOFLO[®]N_o.900UL, Nitto Denko: Osaka, Osaka, Japan, thickness: 0.2 mm) was cut into 35 mm × 70 mm pieces, which were used as fluoropolymer specimens. Six types of unvulcanised rubbers were mixed and prepared using the materials shown in Table 1–6. Sulphur-free

Table 1. Components of sample 1.

Role	Material	Amount [g]
Main component of rubber	Sulfur-free chloroprene rubber (CR)	100
Vulcanisation accelerator	<i>N</i> -(<i>tert</i> -Butyl)-2-benzothiazolesulfenamide (BBS)	0.35
Vulcanisation accelerator aid	Zinc oxide (ZnO)	5
Vulcanisation accelerator aid	Stearic acid	0.5
Reinforcing material	Cellulose powder	30
Plasticizer	Magnesium oxide (MgO)	4
Antioxidant for rubber	<i>N</i> -Phenyl-1-naphthylamine	1

*Vulcanisation condition of Sample 1: 180°C, 20 min

Table 2. Components of sample 2.

Role	Material	Amount [g]
Main component of rubber	Natural rubber (NR)	100
Crosslinking agent	Dicumyl peroxide	1.5
Reinforcing material	Cellulose powder	25

*Vulcanisation condition of Sample 2: 170°C, 6.0 min

Table 3. Components of sample 3.

Role	Material	Amount [g]
Main component of rubber	Natural rubber (NR)	100
Crosslinking agent	Sulfur fine powder	3.5
Vulcanisation accelerator	<i>N</i> -(<i>tert</i> -Butyl)-2-benzothiazolesulfenamide (BBS)	0.7
Vulcanisation accelerator aid	Zinc oxide (ZnO)	6
Vulcanisation accelerator aid	Stearic acid	0.5

*Vulcanisation conditions of Sample 3: 160°C, 5.0 min

Table 4. Components of sample 4.

Role	Material	Amount [g]
Main component of rubber	Natural rubber (NR)	100
Crosslinking agent	Sulfur fine powder	3.5
Crosslinking agent	2-Dibutylamino-4,6-dimercapto-s-triazine	3
Vulcanisation accelerator	<i>N</i> -(<i>tert</i> -Butyl)-2-benzothiazolesulfenamide (BBS)	0.7
Vulcanisation accelerator aid	Zinc oxide (ZnO)	6
Vulcanisation accelerator aid	Stearic acid	0.5

*Vulcanisation conditions of Sample 4: 150°C, 8.0 min

Table 5. Components of sample 5.

Role	Material	Amount [g]
Main component of rubber	Natural rubber (NR)	100
Crosslinking agent	Sulfur fine powder	3.5
Vulcanisation accelerator	<i>N</i> -(<i>tert</i> -Butyl)-2-benzothiazolesulfenamide (BBS)	0.7
Vulcanisation accelerator aid	Zinc oxide (ZnO)	6
Vulcanisation accelerator aid	Stearic acid	0.5
Reinforcing material	Silica powder (SiO ₂)	30

*Vulcanisation condition of Sample 5: 180°C, 4.0 min

Table 6. Components of sample 6.

Role	Material	Amount [g]
Main component of rubber	Natural rubber (NR)	100
Crosslinking agent	Sulfur fine powder	3.5
Crosslinking agent	2-Dibutylamino-4,6-dimercapto-s-triazine	3
Vulcanisation accelerator	<i>N</i> -(<i>tert</i> -Butyl)-2-benzothiazolesulfenamide (BBS)	0.7
Vulcanisation accelerator aid	Zinc oxide (ZnO)	6
Vulcanisation accelerator aid	Stearic acid	0.5
Reinforcing material	Silica powder (SiO ₂)	30

*Vulcanisation condition of Sample 6: 160°C, 4.0 min

chloroprene rubber (CR, M-40, Denka: Chuo-ku, Tokyo, Japan) and natural rubber (NR, Ribbed Smoked Sheet No. 1, Rubber source: Indonesia) were used as the main rubber components. Cellulose powder (CF11, Whatman: Kent, UK) and hydrophilic SiO₂ powder (Nipsil VN3, wet process, Tosoh Silica: Minato-ku, Tokyo, Japan) were used as reinforcing materials. To compare the differences between manufacturing methods, wet and dry processes, hydrophilic SiO₂ powder (HDK®N20, dry process, Wacker Chemie AG: München, Germany), and hydrophobic SiO₂ powder covered with polydimethylsiloxane (HDK®H18, dry process, Wacker Chemie AG) were also used as reinforcing agents. Dicumyl peroxide (Percumyl®D, NOF: Shibuya-ku, Tokyo, Japan), fine sulphur powder (325 Mesh, Hosoi Chemical Industry: Chuo-ku, Tokyo, Japan), and 2-dibutylamino-4,6-dimercapto-s-triazine (Zisnet DB, Sankyo Chemical: Osaka, Osaka, Japan) were used as crosslinking agents. Zinc oxide (JIS Grade No.2, Hokusui Tech: Osaka, Osaka, Japan) and stearic acid (C₁₆:22%–32%, Stearic Acid 50S, New Japan Chemical: Osaka, Osaka, Japan) were used as vulcanisation accelerator aids. *N*-(*tert*-butyl)-2-benzothiazolesulfenamide (Nocceler NS-P, Ouchi Shinko Chemical Industrial: Chuo-ku, Tokyo, Japan) was used as a vulcanisation accelerator. *N*-phenyl-1-naphthylamine (Nocrac PA, Ouchi Shinko Chemical Industrial) was used as an antioxidant for rubber. Sample 1 containing CR was prepared to confirm the effect of chloride on adhesion strength. Note that it was assumed that the chlorides would react with peroxide radicals and/or oxygen-containing functional groups on the heat-assisted plasma-treated PTFE. Sample 2 containing NR and dicumyl peroxide was prepared to confirm the effect of a peroxide crosslinking agent on adhesion strength. The dicumyl peroxide induces the generation of carbon radicals in NR by changing double bonds to single

bonds. It was assumed that the carbon radicals would react with peroxide radicals and/or oxygen-containing functional groups on the heat-assisted plasma-treated PTFE. Sample 3 containing NR and sulphur was prepared to confirm the effect of a sulphur crosslinking agent on adhesion strength. It was assumed that sulphur would react with peroxide radicals and/or oxygen-containing functional groups on the heat-assisted plasma-treated PTFE. Sample 4 containing NR, sulphur, and triazine thiol was prepared to confirm the effect of a thiol crosslinking agent on adhesion strength. It was assumed that the triazine thiols would react with peroxide radicals and/or oxygen-containing functional groups on the heat-assisted plasma-treated PTFE. Sample 5 containing NR, sulphur, and SiO_2 powder was prepared to confirm the effect of SiO_2 powder on adhesion strength. It was assumed that the SiO_2 powder would react with peroxide radicals and/or oxygen-containing functional groups on the heat-assisted plasma-treated PTFE. Sample 6 containing NR, sulphur, triazine thiol, and SiO_2 powder was prepared to confirm the effect of both triazine thiol and SiO_2 powder on adhesion strength.

Method

Plasma treatment

Prior to use, PTFE sheets were sequentially washed with acetone (99.5%, Kishida Chemical: Osaka, Osaka, Japan) and pure water for 1 min each using an ultrasonic bath (USK-1R, AS-ONE: Osaka, 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 then fixed on a cylindrical rotation stage ($L = 34$ mm, $\Phi = 40$ mm).^[15] The stage containing PTFE sample was placed in a custom-made chamber (Meisyo

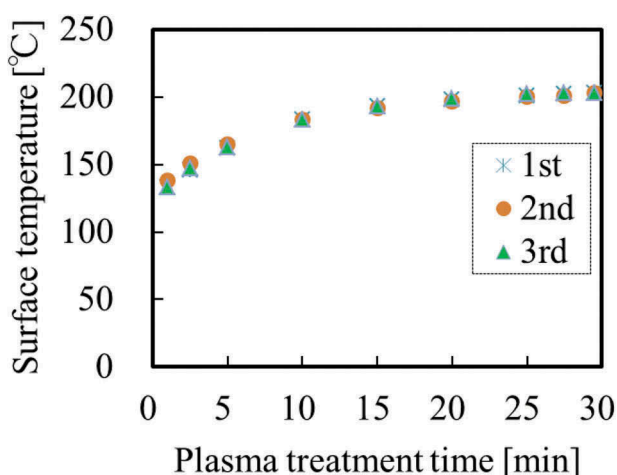


Figure 1. Representative temperature profiles of PTFE surface during heat-assisted plasma treatment for 600 s at 18.7 W/cm^2 three times.

Kiko: Tanba, Hyogo, Japan) with the vacuum system.^[20] The reactor pressure was decreased to below 10 Pa using a rotary pump (GDH-361, Shimadzu: Kyoto, Kyoto, Japan) then helium gas (He, 99.99%, Iwatani Fine Gas) was introduced until the atmospheric pressure (101300 Pa). Plasma was generated between two electrodes using a 13.56 MHz radio frequency (RF) generator in the chamber filled with He gas without flowing. All the PTFE sheets were heat-assisted plasma-treated for 600 s at 18.7 W/cm². The surface temperature of the PTFE samples during plasma treatment was measured with a digital radiation thermometer system (FT-H40K and FT-50A, Keyence: Osaka, Osaka, Japan). Figure 1 shows the representative temperature profiles of PTFE surface three times. It was confirmed that all the maximum surface temperatures were above 200°C. All the error of temperature profiles three times were within 5°C, which indicates high reproducibility. Effect of surface temperature on adhesion strength of PTFE were previously studied and reported.^[14,15] When surface temperature of PTFE during plasma treatment was lower than 100°C, the adhesion strength of plasma-treated PTFE/IIR was below 0.2 N/mm. In contrast, when surface temperature of PTFE during plasma treatment was higher than 200°C, the adhesion strength of plasma-treated PTFE/IIR was above 2.0 N/mm and cohesion failure of IIR occurred. According to these reports, plasma condition (for 600 s at 18.7 W/cm²) in this study was chosen to be at higher than 200°C.

Prior to adhesion strength test, confirmation of surface chemical composition using a Quantum 2000 instrument (Ulvac-Phi: Chigasaki, Kanagawa, Japan), confirmation of generation of peroxide radicals (C–O–O[•]) using a JES-FA100x (JEOL: Akishima, Tokyo, Japan), and adhesion confirmation test of heat-assisted plasma-treated PTFE for 600 s at 18.7 W/cm² were performed. Although only the peak attributed to CF₂ was observed at ca. 292 eV for as-received PTFE in Figure 2, the intensity of the peak attributed to fluorine-containing functional groups (CF₃, CF₂, C–F) decreased and the intensities of the peaks attributed to oxygen-containing functional groups

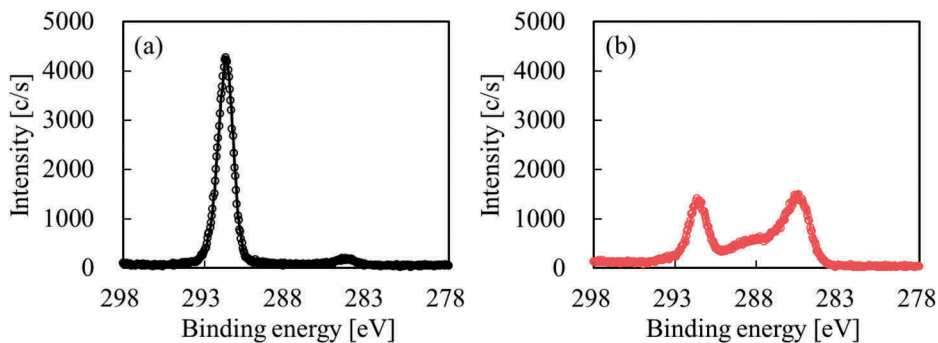


Figure 2. Representative C1s-XPS spectra of PTFE samples (a) before and (b) after heat-assisted plasma treatment for 600 s at 18.7 W/cm².

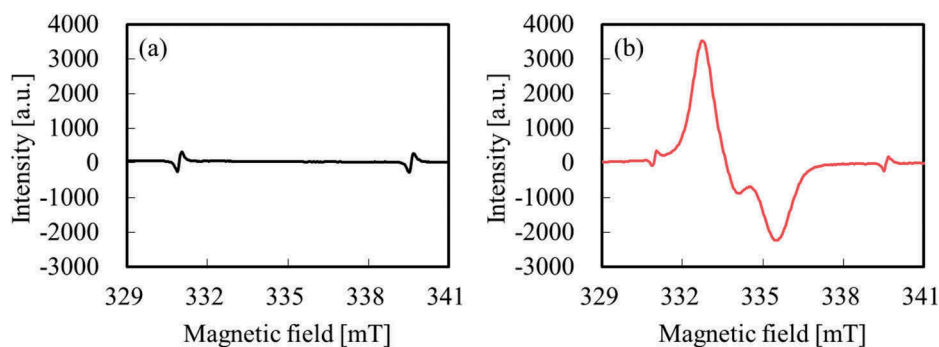


Figure 3. Representative ESR spectra of PTFE samples (a) before and (b) after heat-assisted plasma treatment for 600 s at 18.7 W/cm^2 .

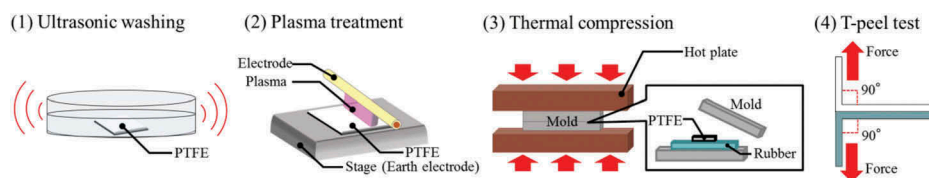


Figure 4. Schematic diagram of the sample preparation sequence for the adhesion test.

(O–C=O, C=O, C–O) and carbon groups (C–C, C=C) increased in [Figure 2](#) as compared to those of the as-received PTFE upon heat-assisted plasma treatment. Although only the peaks attributed to Mn^{2+} markers were observed at ca. 331 and 340 mT for as-received PTFE in [Figure 3](#), the peak attributed to alkyl-type peroxide radicals ($-\text{CF}_2\text{CFOO}^*\text{CF}_2-$) was detected upon heat-assisted plasma treatment in [Figure 3](#). These behavior in this study were consistent with those in previous reports.^[14,15] It is previously reported that oxygen-containing functional groups and peroxy radicals generate when fluoropolymers plasma-treated using noble gas is exposed to the air.^[21] In addition, the plasma-treated PTFE/IIR was also above 2.0 N/mm and cohesion failure of IIR also occurred. As a result, it was confirmed that this plasma condition had no problems. Plasma treatment was performed only on the PTFE surface and not on the unvulcanised rubber surface.

Adhesion strength test

[Figure 4](#) shows a schematic diagram of the general sequence for the adhesion test. First, the plasma-treated PTFE samples were placed on unvulcanised rubber sheets in a mould. Second, the assembly samples were compressed at appropriate temperatures and times for each type of unvulcanised rubber because of complete crosslinking occurring when using a hot-pressing machine (AH-2003, AS-ONE). Each vulcanisation time was confirmed via

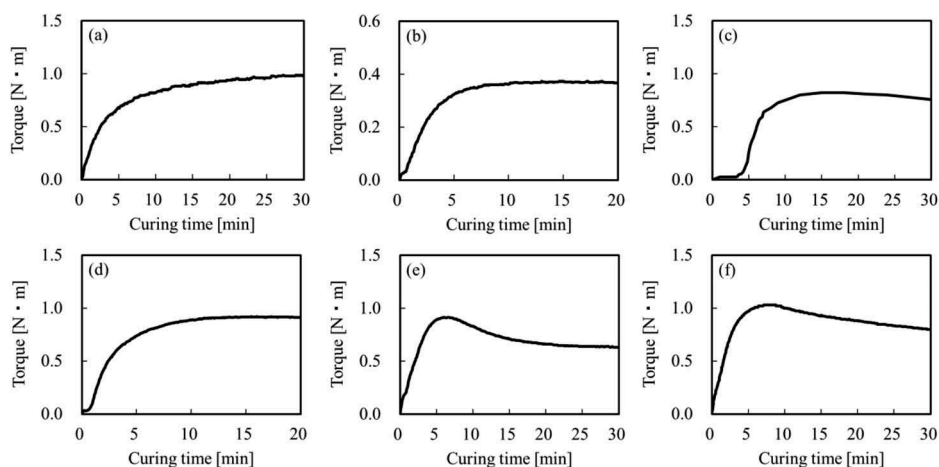


Figure 5. Results of the vulcanisation judgement test for confirmation of proper vulcanisation time. (a) Sample 1 at 180°C, (b) sample 2 at 170°C, (c) Sample 3 at 160°C, (d) Sample 4 at 150°C, (e) Sample 5 at 180°C, and (f) Sample 6 at 160°C.

a vulcanisation judgement test using a rubber testing machine (Curelasterometer type V, Orientec; Toyoshima-ku, Tokyo, Japan), as shown in Figure 5. Here no adhesives were used in the adhesion process. Third, the rubber/PTFE assembly was returned to room temperature. Fourth, the adhesion strengths of the rubber/PTFE assembly was measured with a T-peel test using a universal testing device (AG-1000D, Shimadzu) and/or combination of a digital force gauge (ZP-200N, Imada; Toyohashi, Aichi, Japan) and an electric-driven stand (MX-500N, Imada). Finally, the adhesion strengths were calculated by dividing the average tensile strength by the width of the rubber/PTFE assembly (ca. 10 mm). Three samples were prepared under the same conditions to confirm the reproducibility.

Surface chemical composition analysis

XPS measurements were conducted with a scanning XPS microprobe (PHI5000VersaProbeII, Ulvac-Phi) attached to a monochromated Al-K α source. The XPS spectra were obtained at a take-off angle of 45°. The area of X-ray irradiation was $\Phi = 100 \mu\text{m}$, the pass energy was 11.75 eV, and the step size was 0.05 eV. C1s-XPS and Si2p-XPS spectra were collected from 280 to 296 eV and from 95 to 110 eV, respectively. The cumulative number of the measurements was five. During a XPS measurement, the low-speed electron beam and an Ar ion beam were used to irradiate the measured samples to neutralise their charges.

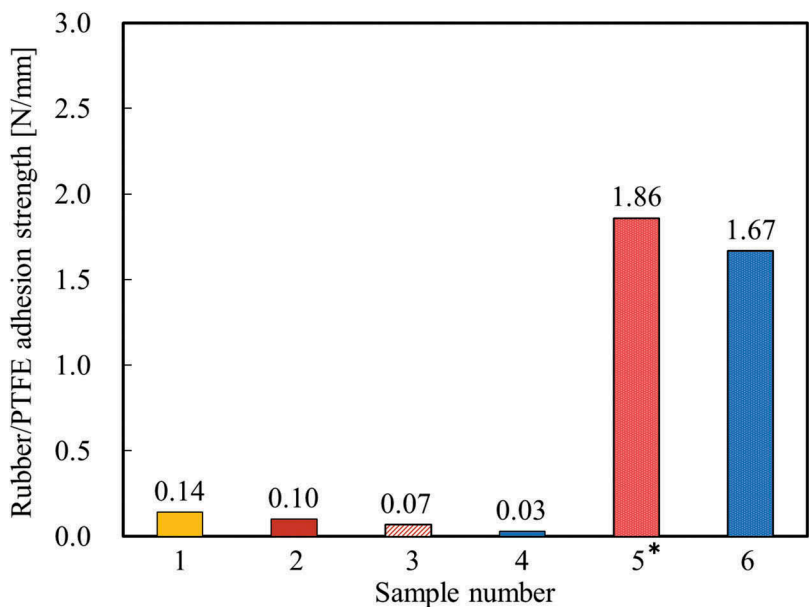


Figure 6. Adhesion strength between the heat-assisted plasma-treated PTFE and rubber for samples 1–6 prepared as shown in Table 1–6. no adhesives were used. * indicates that cohesion failure of rubber occurred in the middle of a T-peel test.

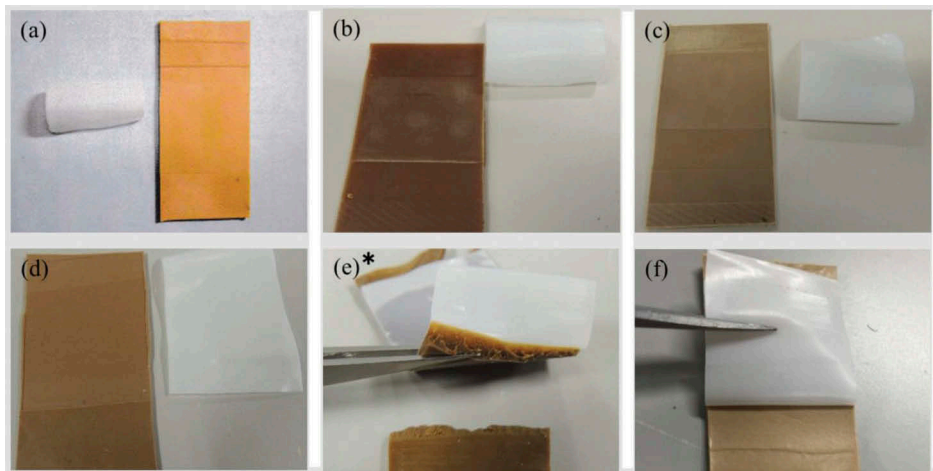


Figure 7. Photographs of samples 1–6 after T-peel test. (a) sample 1, (b) sample 2, (c) sample 3, (d) sample 4, (e) sample 5, and (f) sample 6. * indicates that cohesion failure of rubber occurred in the middle of a T-peel test.

Results and discussion

Adhesion strength between plasma-treated PTFE and rubber

Figure 6 shows the adhesion strength between plasma-treated PTFE and rubber Samples 1–6. Figure 7 shows the photographs of Samples 1–6 after

the T-peel test. For Sample 1, the adhesion strength was 0.14 N/mm and the rubber was easily peeled (Figure 7a). This indicates that chlorides do not interact with peroxide radicals and/or oxygen-containing functional groups on heat-assisted plasma-treated PTFE. For Sample 2, the adhesion strength was 0.10 N/mm and the rubber was easily peeled (Figure 7b). This indicates that carbon radicals do not interact with peroxide radicals and/or oxygen-containing functional groups on heat-assisted plasma-treated PTFE. For Sample 3, the adhesion strength was 0.07 N/mm and the rubber was easily peeled (Figure 7c). This indicates that the sulphur does not interact with peroxide radicals and/or oxygen-containing functional groups on the heat-assisted plasma-treated PTFE. For Sample 4, the adhesion strength was 0.03 N/mm and the rubber was also easily peeled (Figure 7d). This indicates that triazine thiols do not interact with peroxide radicals and/or oxygen-containing functional groups on heat-assisted plasma-treated PTFE. For Sample 5, the adhesion strength was 1.86 N/mm and cohesion failure of rubber occurred (Figure 7e). This indicates that SiO₂ powder interacts with peroxide radicals and/or oxygen-containing functional groups on heat-assisted plasma-treated PTFE. For Sample 6, the adhesion strength was 1.67 N/mm and the rubber was difficult to peel but cohesion failure of rubber did not occur (Figure 7f). The adhesion strength of Sample 6 (1.67 N/mm) was much higher than that of Sample 4 (0.04 N/mm) but slightly lower than that of Sample 5 (1.86 N/mm). These results indicate that the SiO₂ powders positively affect the adhesion strength, but the triazine thiols negatively affect the adhesion strength.

To confirm the additive effect of SiO₂ powder on the adhesion strength, NR samples were prepared with different amounts of added SiO₂ in the range 0–40 g to 100 g NR. This component is shown in Table 7. Except for SiO₂, other components and their amounts for Table 7 are the same as in Sample 5 (Table 5). Figure 8 shows the adhesion strength between the heat-assisted plasma-treated PTFE and NR samples prepared with different amounts of SiO₂. The adhesion strength increased with increasing the amount of SiO₂ and cohesion failure of NR occurred when 30 and 40 g SiO₂ were added. It is confirmed that the addition of SiO₂ powder to NR affected the adhesion strength.

Table 7. Components of NR with different amounts of SiO₂.

Role	Material	Amount [g]
Main component of rubber	Natural rubber (NR)	100
Crosslinking agent	Sulfur fine powder	3.5
Vulcanisation accelerator	<i>N</i> -(<i>tert</i> -Butyl)-2-benzothiazolesulfenamide (BBS)	0.7
Vulcanisation accelerator aid	Zinc oxide (ZnO)	6
Vulcanisation accelerator aid	Stearic acid	0.5
Reinforcing material	Silica powder (SiO ₂)	0, 10, 20, 30, 40

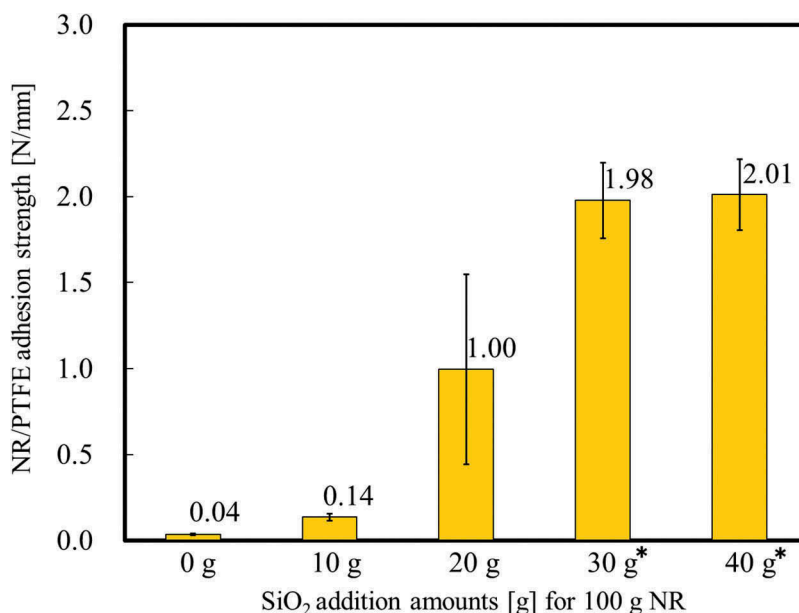


Figure 8. Adhesion strength between the heat-assisted plasma-treated PTFE and NR samples prepared with different amounts of SiO₂ as shown in Table 7. * indicates that cohesion failure of rubber occurred in the middle of a T-peel test.

Confirmation of reaction between plasma-treated PTFE and SiO₂ powder using XPS

To confirm the reaction between plasma-treated PTFE and SiO₂ powder, a direct reaction was observed in the absence of all the NR components except for SiO₂ powder. First, SiO₂ powder was directly thermally compressed to heat-assisted plasma-treated PTFE sheet at almost 10 MPa at 180°C for 10 min using a compression moulding machine (NF-50, Shinto Metal Industries), as shown in Figure 9a. Second, the unreacted SiO₂ powder on the plasma-treated PTFE was removed by washing with tap water for ca. 20 s and with distilled water for ca. 10 s, followed by ultrasonic washing in distilled water for 5 min; each wash was repeated more than four times (Figure 9b). Finally, XPS measurements were conducted. Prior to the XPS measurements, all the samples were dried using an air gun. For comparison, a reference sample was prepared using as-received PTFE via the process shown in Figure 9.

Figure 10 shows the XPS spectra of the PTFE surface after thermal compression with SiO₂ powder (VN3). Although only the peak attributed to CF₂ was observed at ca. 292 eV for as-received PTFE, the intensity of the peak attributed to fluorine-containing functional groups (CF₃, CF₂, C–F) decreased and the intensities of the peaks attributed to oxygen-containing functional groups (O–C=O, C=O, C–O) and main carbon groups (C–C, C–H, C=C) increased as compared to those of the

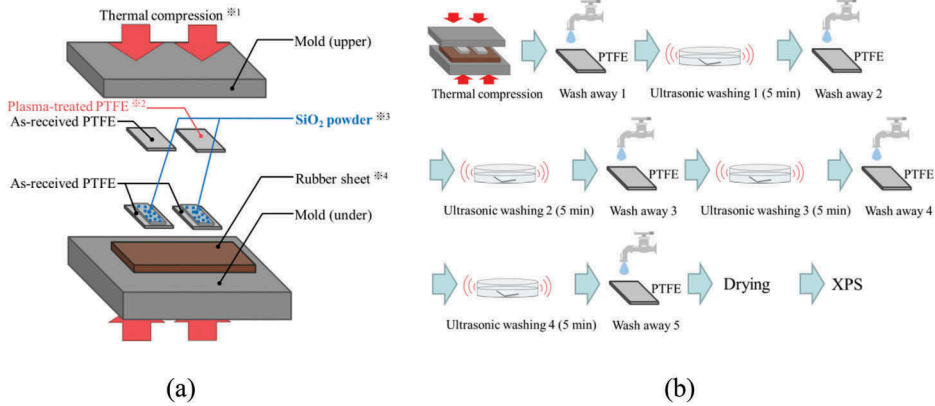


Figure 9. Schematic diagram of the sequence for confirming the reaction between plasma-treated PTFE and SiO₂ powder using XPS. (a) before thermal compression, (b) after thermal compression. *¹ Thermal compression was performed at almost 10 MPa at 180°C for 10 min. *² Heat-assisted plasma treatment was performed for 600 s at 18.7 W/cm². *³ Three types of SiO₂ powders: VN3, H18, and N20 were used. *⁴ A vulcanised rubber having high heat-resistance was used as a cushion.

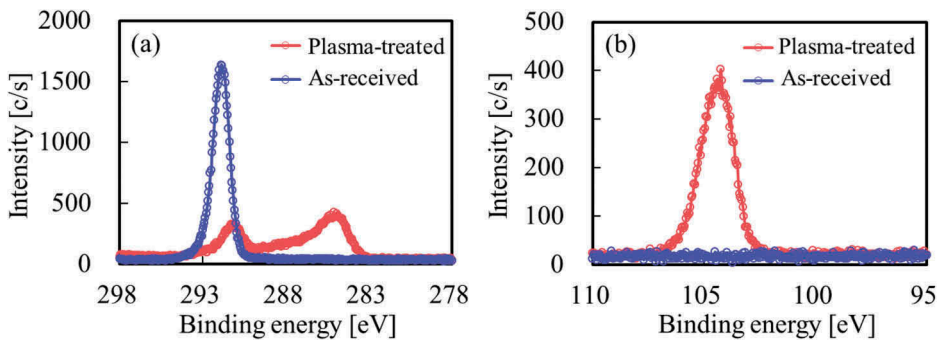


Figure 10. XPS spectra of the PTFE surface after thermal-compression with hydrophilic SiO₂ powder (VN3) (a) C1s, (b) Si2p.

as-received PTFE upon heat-assisted plasma treatment, as shown in the C1s-XPS spectra (Figure 10a). As a result, surface modification of PTFE via heat-assisted plasma treatment was confirmed. Si was detected on the plasma-treated PTFE but not the as-received PTFE by Si2p-XPS spectrum (Figure 10b). These results indicated that SiO₂ powder remained on the plasma-treated PTFE surface despite repeated washing. In addition, the strong adhesion of SiO₂ powder implied that this chemically reacted with the plasma-treated PTFE surface.

To compare the effect of wettability of SiO₂ surface on adhesion to PTFE, hydrophobic SiO₂ powder (H18), which was prepared through a dry process, was used for the same confirmation test. Figure 11 shows the XPS spectra of the PTFE surface after thermal compression with hydrophobic SiO₂ powder

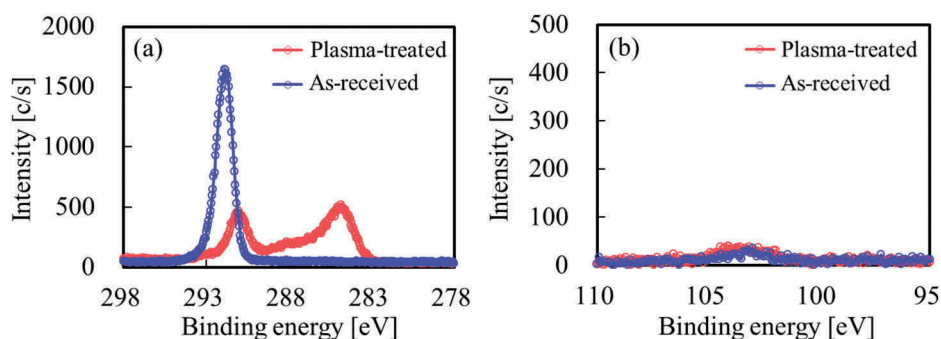


Figure 11. XPS spectra of the PTFE surface after thermal-compression with hydrophobic SiO_2 powder (H18) (a) C1s, (b) Si2p.

(H18). Figure 11a as well as Figure 10a indicates surface modification of PTFE via heat-assisted plasma treatment. In contrast, Si was barely detected in either the as-received or the plasma-treated PTFE via Si2p-XPS spectra (Figure 11b). These results indicated that hydrophobic SiO_2 powder barely remained on the plasma-treated PTFE surface as there was no interaction between both materials.

VN3 is a hydrophilic SiO_2 powder prepared through a wet process, whereas H18 is a hydrophobic SiO_2 powder prepared through a dry process. Taking the manufacturing method of SiO_2 powder into account, hydrophilic SiO_2 powder (N20), which was prepared through a dry process, was used for the same confirmation test. Figure 12 shows the XPS spectra of the PTFE surface after thermal compression with hydrophilic SiO_2 powder (N20). Figure 12a as well as Figures 10a and 11a indicates surface modification of PTFE via heat-assisted plasma treatment. Si was detected in the plasma-treated PTFE but not the as-received PTFE via the Si2p-XPS spectra in Figure 12b as well as Figure 10b.

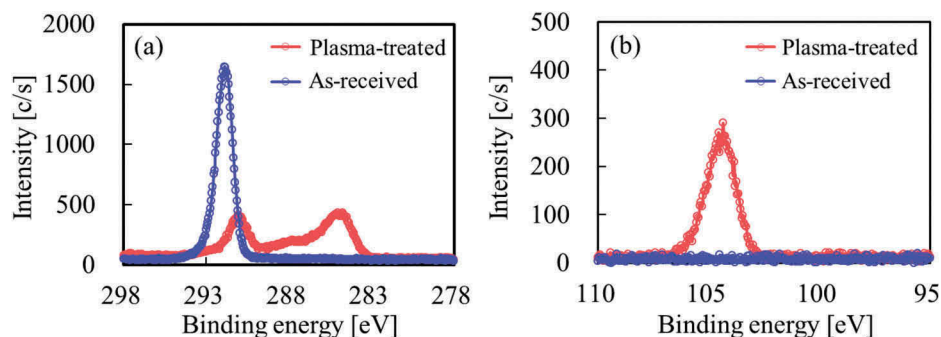
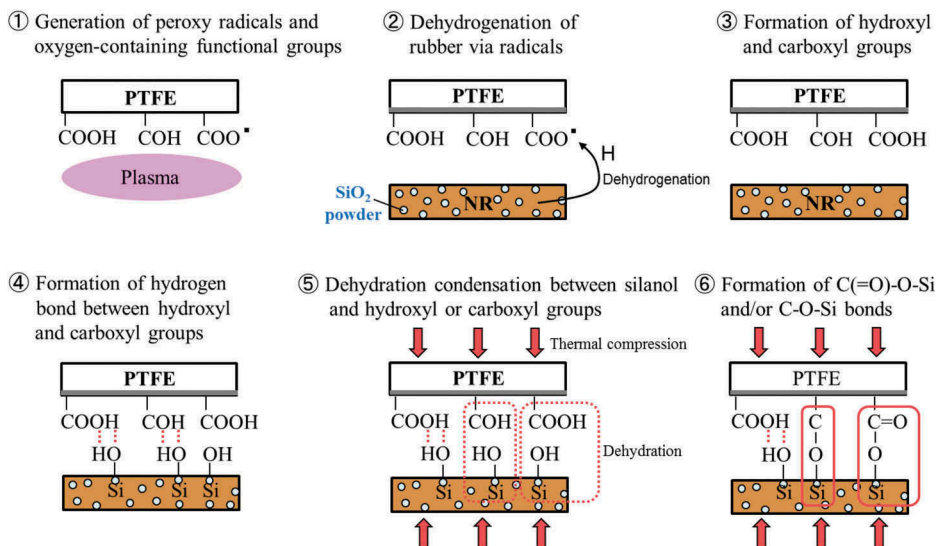


Figure 12. XPS spectra of the PTFE surface after thermal-compression with hydrophilic SiO_2 powder (N20) (a) C1s, (b) Si2p.

Table 8. Atomic ratios of the PTFE surface after thermal compression with SiO₂ powder, which calculated from each survey XPS spectrum.

Sample condition	C1s	O1s	F1s	Si2p
VN3/PTFE(as-received)	30.3	0.2	69.6	0.0
VN3/PTFE(plasma-treated)	34.5	33.6	22.4	9.5
H18/PTFE(as-received)	29.2	0.8	69.8	0.2
H18/PTFE(plasma-treated)	54.5	10.2	34.6	0.8
N20/PTFE(as-received)	31.2	0.2	68.6	0.0
N20/PTFE(plasma-treated)	36.6	18.6	40.2	4.6

The atomic ratios of the PTFE surface after thermal compression with SiO₂ powder were calculated from the survey XPS spectra, as shown in Table 8. For all as-received PTFE, the Si atomic ratios were lower than 1%. In contrast, for plasma-treated PTFE except addition of hydrophobic SiO₂ (H18), the Si atomic ratios were higher than 4.5%. Although two types of hydrophilic SiO₂ powder (VN3 and N20) strongly adhered to the plasma-treated PTFE surface, hydrophobic SiO₂ powder (H18) did not adhere. The difference indicates that silanol groups (Si-OH) of the SiO₂ surface affect the adhesion strength between the plasma-treated PTFE and rubber. A proposed model for strong adhesion is shown in Figure 13. First, peroxy radicals and oxygen-containing functional groups (C(=O)-OH, C-OH) are generated upon plasma treatment. Second, peroxy radicals on the plasma-treated PTFE may induce the dehydrogenation of rubber. Third, hydroxyl and carboxyl groups are generated regardless of the presence or absence of the second step: dehydrogenation of rubber. Fourth, hydrogen bonds are formed between hydroxyl and carboxyl

**Figure 13.** Proposed model for strong adhesion between heat-assisted plasma-treated PTFE and rubber containing SiO₂ powder.

groups on the PTFE surface and silanol groups of the SiO_2 powder on the rubber surface. Fifth, dehydration condensation occurs between silanol and hydroxyl or carboxyl groups. Finally, C–O–Si and/or C(=O)–O–Si bonds are formed. Considering that NR cohesion failure occurred when SiO_2 powder was added, it is reasonable to suppose that covalent bonds as well as hydrogen bonds are formed.

Conclusion

We prepared six types of rubbers to clarify the effects of rubber compounding agent on adhesion strength between rubber and heat-assisted plasma-treated PTFE. It was found that addition of SiO_2 powder to rubber was particularly effective for improving the adhesion strength. The adhesion strength increased with increasing the amount of SiO_2 , and the cohesion failure of rubber occurred when the amount of SiO_2 was more than 30 g to 100 g NR. In addition, it was confirmed that hydrophilic SiO_2 powder strongly adhered to the heat-assisted plasma-treated PTFE surface. We proposed a model of high adhesion strength upon addition of SiO_2 powder. This simple method of adding SiO_2 powder could be applied not only to rubber but also to various polymers to improve their adhesion to heat-assisted plasma-treated fluoropolymers.

Acknowledgments

The study was supported by a grant from the Japan Society for the Promotion of Science (JSPS KAKENHI Grant Number 15K05723).

Funding

This work was supported by the Japan Society for the Promotion of Science [JSPS KAKENHI Grant Number 15K05723].

ORCID

Yuji Ohkubo  <http://orcid.org/0000-0001-7366-5108>

References

- [1] Schonhorn, H.; Hansen, R. H. *J. Appl. Polym. Sci.* 1967, 11, 1461–1474.
- [2] Bikerman, J. J.; *Ind. Eng. Chem.* 1967, 59, 40–44.
- [3] Marchesi, J. T.; Keith, H. D.; Garton, A. J. *Adhesion*. 1992, 39, 185–205.
- [4] Okubo, M.; Tahara, M.; Aburatani, Y.; Kuroki, T.; Hibino, T. *IEEE Trans. Ind. Appl.* 2010, 46, 1715–1721.

- [5] Inagaki, N.; Tasaka, S.; Umehara. *J. Appl. Polym. Sci.* 1999, 71, 2191–2200.
- [6] Kim, S. R.; *J. Appl. Polym. Sci.* 2000, 77, 1913–1920.
- [7] Seo, Y.; Kim, S.; Kim, H.; Kim, J. *Langmuir*. 2005, 21, 3432–3435.
- [8] Rodriguez-Santiago, V.; Bujanda, A. A.; Stein, B. E.; Pappas, D. D. *Plasma Process. Polym.* 2011, 8, 631–639.
- [9] Watanabe, T.; Iwao, T.; Yumoto, M. *IEEEJ Trans. Fund. Mater.* 2012, 132, 245–250.
- [10] Kang, E. T.; Zhang, Y. *Adv. Mater.* 2000, 12, 139–150.
- [11] Zhang, M. C.; Kang, E. T.; Neoh, K. G.; Tan, K. L. *Colloid. Surf. A.* 2001, 176, 139–150.
- [12] Zhang, L.; Chen, Y.; Dong, T. *Surf. Interface Anal.* 2004, 36, 311–316.
- [13] Takata, R.; Nagasaka, Y.; Li, Q.; Iwao, T.; Yumoto, M. *IEEEJ Trans. Fund. Mater.* 2015, 135, 41–46.
- [14] Ohkubo, Y.; Ishihara, K.; Sato, H.; Shibahara, M.; Nagatani, A.; Honda, K.; Endo, K.; Yamamura, K. *RSC Adv.* 2017, 7, 6432–6438.
- [15] Ohkubo, Y.; Ishihara, K.; Shibahara, M.; Nagatani, A.; Honda, K.; Endo, K.; Yamamura, K. *Sci. Rep.* 2017, 7, 9476.
- [16] Tsai, Y. M.; Boerio, F. J.; Kim, D. K. *J. Adhesion*. 1997, 61, 247–270.
- [17] Cho, P. L.; Jeon, G. S.; Ryu, S. K.; Seo, G. *J. Adhesion*. 1999, 70, 241–258.
- [18] Jeon, G. S.; Han, M. H.; Seo, G. *J. Adhesion Sci. Technol.* 1999, 13, 153–168.
- [19] Jayaseelan, S. K.; Van Ooij, W. J. *J. Adhesion Sci. Technol.* 2001, 15, 967–991.
- [20] Yamamoto, Y.; Akiyama, H.; Ooka, K.; Yamamura, K.; Oshikane, Y.; Zettsu, N. *Curr. Appl. Phys.* 2012, 12, S63–S68.
- [21] Momose, Y.; Tamura, Y.; Ogino, M.; Okazaki, S.; Hirayama, M. *J. Vac Sci. Technol. A.* 1992, 10, 229–238.