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Effect of surface treatment using non-thermal atmospheric pressure plasma jet on dissimilar material direct joining using Polyetheretherketone

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ABSTRACT

Polyetheretherketone (PEEK) is widely used as a biomaterial due to its excellent mechanical strength and biocompatibility. However, its bioinert surface and poor adhesion to metallic materials, such as titanium, often limit its performance in implant applications. To address these issues, this study investigated the influence of atmospheric-pressure radio-frequency (RF) plasma treatment on the surface of PEEK, aiming to improve both its interfacial bonding with pure titanium TP340 (JIS H4600 TP340, ASTM B265 Grade 2) and biological response. The plasma treatment effectively introduced oxidation-induced functional groups—such as O–C=O—onto the PEEK surface and successfully eliminated cracks and voids, commonly referred to as "weak bonding layers," which typically form during the molding process of PEEK materials. These surface modifications resulted in a marked enhancement in tensile shear strength when PEEK was directly bonded to TP340. Comprehensive surface characterizations employing XPS, AFM, and SEM verified the presence of both chemical and topographical alterations that contributed to improved interfacial bonding. Notably, the elimination of weak bonding layers on the PEEK surface played a pivotal role in augmenting bond strength. Furthermore, in vitro biological evaluations using MC3T3-E1 osteoblast-like cells revealed significantly enhanced cell adhesion and proliferation on plasma-treated PEEK surfaces in comparison to untreated PEEK.

1. Introduction

Polyetheretherketone (PEEK) is a polymeric material that has attracted the attention of researchers because of its excellent properties such as high mechanical strength, thermal stability (beyond 300 °C), and chemical resistance in corrosive environments, which can be used in many applications [1]. PEEK has been used in orthopedic implants since the 1980s in dental and medical applications because it is an inert polymer with excellent mechanical properties and biocompatibility [2–4]. One of the reasons PEEK is used in a wide range of biomedical applications is that the presence of ketone groups in the molecular structure of PEEK allows its surface to be more modified. On the other hand, the problem with PEEK is that phenomena such as osseointegration do not occur between PEEK and bone, which can lead to implant stability problems, complications, and the need for additional surgery [5]. PEEK exhibits a glass transition temperature of 145 °C and a melting temperature of 340 °C. Owing to its semi-crystalline nature, it demonstrates minimal thermal degradation at elevated temperatures, thereby permitting continuous operation at 250 °C for up to 20,000 h [6]. These thermal and mechanical properties make PEEK a promising candidate for long-term biomedical and industrial applications.

Recently, new developments in CFR-PEEK, a carbon fiber reinforced plastic with PEEK as the matrix material, have made it an attractive candidate for biomedical applications since it has been reported that carbon fibers can further enhance mechanical and wear properties [7]. For this reason, carbon fiber reinforced PEEK (CFR-PEEK), which has high specific strength and excellent thermal shock resistance, is beginning to be used in load-bearing structures [8–10] such as aircraft frames [11]. CFR-PEEK is also attracting attention in medical applications. In total joint replacement (TJR) surgery, a damaged joint is removed and

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replaced with a metal, plastic, or ceramic joint device. In the case of the joint device made of metal, metal load-bearing components tend to shield stresses, resulting in bone resorption due to the mismatch in elastic modulus between the implant and the surrounding bone. Therefore, as an alternative material to metal, the majority of total joint replacements use ultra-high molecular weight polyethylene (UHMWPE) bearings; however, wear, oxidation, and fatigue failure in the body are challenges [12–16].

The use of CFR-PEEK in TJRs has the following advantages over UHMWPE and metal-based biomaterials. PEEK is known to maintain its mechanical properties up to a certain number of treatment cycles in commonly employed sterilization processes (gamma radiation, steam autoclave, vaporized hydrogen peroxide, ethylene oxide, etc.) [17,18]. Furthermore, using CFR-PEEK as a load-bearing material to replace metal components has the potential to reduce stress shielding and bone resorption, as its elastic modulus more closely resembles bone [19], while also addressing concerns about long-term metal implantation in the body.

Furthermore, the hybrid materials consisting of Ti / Ti alloys and PEEK / CFR-PEEK are required in medical devices. The hybrid materials synergistically integrate the superior osseointegration properties of Ti / Ti alloys with the biomechanical compatibility of PEEK / CFR-PEEK, delivering a balanced performance in medical devices that is challenging to attain with monolithic materials. This composite strategy mitigates the risks associated with stress shielding and nonunion, while simultaneously enhancing the efficacy of postoperative diagnostic imaging, thereby facilitating improved clinical outcomes for patients [20]. In a cage device for spinal fusion surgery, this same Ti/PEEK composite interbody device was evaluated for anterior lumbar interbody fusion (ALIF) by R.J. Mobbs [21]. Coating the surface of PEEK with Ti, which is biocompatible and osteoconductive, not only improves its biological activity but also maintains its elastic modulus [22].

When exposed to the atmosphere, titanium forms a stable natural oxide film of titanium dioxide on its surface, which exhibits excellent biocompatibility [23]. Based on these results, Ti or TiO_2 coatings have been used on PEEK to improve the bonding efficiency with bone implants [24]. In general, the primary direct bonding mechanism between metals and polymers is considered to be hydrogen bonding between oxides on the metal surface and polar functional groups on the polymer material surface. For achieving strong bonding with PEEK/CFR-PEEK and Ti/Ti alloys, the addition of functional groups to the polymer surface, the removal of surface contamination, and the formation of a stable oxide film on the metal are crucial [25,26].

When evaluating the adhesion between CFR-PEEK and metals, the primary bonding occurs between the PEEK matrix and the metal surface. Understanding this interfacial bonding mechanism is essential for achieving strong adhesion, and surface treatment is necessary to promote stable bonding [25,26]. Surface modification for direct bonding currently includes wet treatment using acids and alkalis [27] and dry treatment such as UV irradiation [28], corona treatment [29], and plasma treatment [30]. Among them, plasma treatment is superior in that it can efficiently modify surfaces by irradiating materials with oxygen radical species [31]. In addition to plasma and wet-chemical treatments, mechanical–chemical surface modification methods such as the Rocatec process have been used to promote polymer–metal adhesion through silica coating and silane coupling, forming more stable covalent bonds at the interface. However, these processes require multiple treatment steps and additional coating materials, which may complicate the fabrication of hybrid biomedical devices. In contrast, atmospheric-pressure plasma treatment can directly activate the PEEK surface in a dry and clean manner without introducing intermediate layers, making it more suitable for achieving direct, contamination-free bonding in implant applications.

As one of the surface modifications before direct bonding, plasma treatments using an atmospheric-pressure radio-frequency (RF) plasma jet have been proposed. In our previous study, aluminum alloys A1050, A5052, and pure titanium TP340 (JIS H4600 TP340/ASTM B265 Grade 2) to the PEEK were directly joined by surface pretreatment with atmospheric pressure RF plasma jets and hot-pressing method, and the effect of plasma treatment to metals, including A1050, A5052, and TP340, on joint strength to PEEK have been confirmed [31–33].

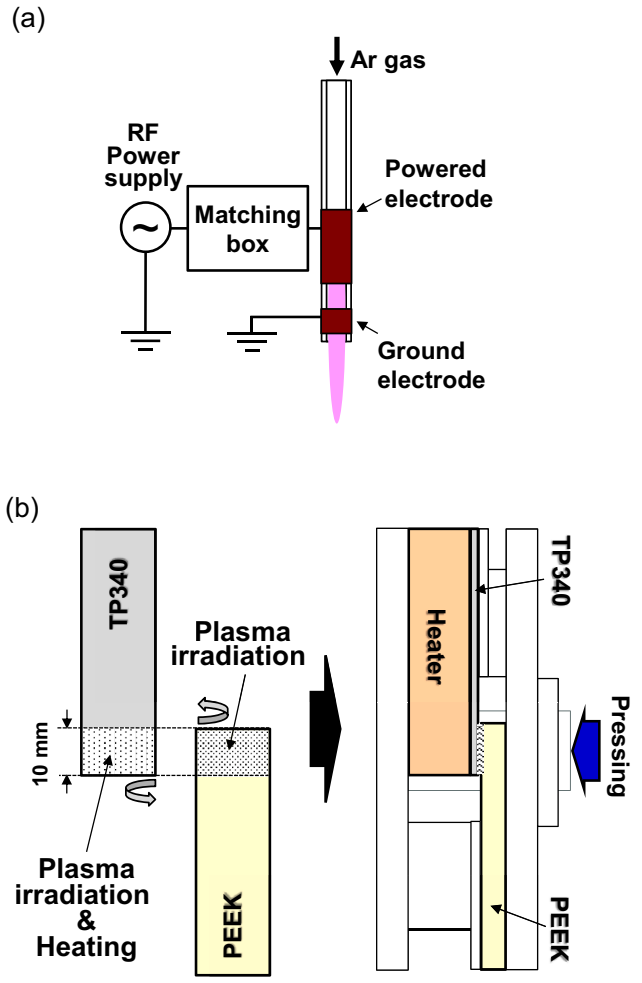

Fig. 1. Schematic illustrations of (a) an atmospheric pressure RF plasma jet and (b) joining procedure of dissimilar metal-organic materials using an atmospheric pressure plasma jet.

Furthermore, the investigation into the effect of metal surface roughness revealed that the addition of functional groups exerts a greater influence on bond strength than surface roughness [34]. Plasma irradiation of PEEK has been shown to increase bonding strength, with longer irradiation times generally enhancing interfacial adhesion with metals [31–34]. However, the precise modifications induced by plasma treatment on the PEEK surface, as well as the underlying mechanisms responsible for the enhancement of bond strength, remain insufficiently elucidated. Despite the potential advantages of PEEK and Ti hybrid materials in biomedical applications, the weak interfacial bonding between PEEK and metals and the insufficient biological activity of PEEK remain major obstacles for their practical use as implant materials. Plasma surface modification is a promising method to address these issues; however, the detailed mechanisms by which plasma treatment improves both bonding strength and biocompatibility have not been fully understood. Therefore, this study was undertaken to clarify how atmospheric-pressure plasma treatment modifies the PEEK surface at the physical and chemical levels, and how these modifications enhance both interfacial adhesion and cellular response. The specific aim of this work is to elucidate the mechanism by which plasma treatment improves the

bonding strength between PEEK and titanium, as well as the biocompatibility of the PEEK surface. It is hypothesized that plasma treatment enhances bonding and biological performance through two main effects: (1) the introduction of oxygen-containing functional groups (such as O–C=O) that promote interfacial chemical bonding, and (2) the removal of weakly bonded surface layers formed during the molding process, thereby improving mechanical adhesion and supporting better cell attachment and proliferation.

In this paper, the effect of plasma irradiation of PEEK on the physical and chemical state of the PEEK surface in PEEK-metal direct bonding was investigated. Furthermore, the biocompatibility of plasma-treated PEEK was determined by in vitro evaluation using osteoblast-like cells to investigate its potential for implant materials.

2. Experimental procedures

2.1. Surface treatment by atmospheric pressure RF plasma jets

The PEEK test pieces (Mitsubishi chemical advanced materials, Ketron 1000, melting temperature: 340 °C) were 500 mm × 15 mm × 5 mm, and the titanium TP340 sheet test pieces (JIS H4600 TP340/ASTM B265 Grade 2, Kobe Steel, Ltd) used were 500 mm × 15 mm × 1.5 mm.

A radio-frequency (RF) excited Ar plasma jet was generated by two metal strips, one 15 mm long and the other 5 mm wide, wound around a quartz tube at 5 mm intervals as the power and ground electrodes, respectively, as schematically shown in Fig. 1(a) [35,36]. The narrow ground electrode was positioned at the head of the quartz tube, and the wide power electrode was set 5 mm away from the edge of the ground electrode. The outer and inner diameters of the quartz tube were 6 and 4 mm, respectively. Sine-wave voltages of frequencies 60 MHz were applied to the power electrode. The RF power varied from 30 W (The peak-to-peak voltage, V_{pp} = 1.1 kV) to 78 W (V_{pp} = 1.6 kV), and the Ar gas flow rate was fixed at 3slm. During plasma treatment, the plasma jet was scanned across the entire surface of the PEEK specimens to ensure uniform exposure. The irradiation time refers to the total duration of plasma exposure on the surface.

All samples that had not undergone plasma treatment were used in their as-received condition. The surface temperature of PEEK surfaces during plasma treatment was measured in situ using an infrared thermometer (MICRO-EPSILON, thermoMETER: 3MH—CF3-CB3, Ortenburg, Germany).

2.2. Tensile shear tests

Fig. 1(b) shows the procedure for joining dissimilar materials of metal and polymer using an atmospheric-pressure RF plasma jet. As a pre-treatment for the bonding process, the polymer surface was treated with an atmospheric-pressure RF plasma jet. The metal surface was heated using a heater until it reached the melting point of PEEK (340 °C), after which the polymer and metal were joined by heat pressing. The polymer was pressed against the metal under a joining pressure of 14 kN, and the process was completed upon verification of the initial melting of the polymer. The joint configuration in the overlap joint is shown in Fig. 1(b). An overlap between the two materials was set to 10 mm. Tensile shear tests of the joints were performed to measure the bond strength. To evaluate the tensile shear strength of the joint, a tensile load was applied parallel to the bonding interface of the joined specimen, and the load at which shear failure occurred was recorded. A tensile tester was used for the tensile shear tests (Autograph AGS-X, Simadzu Corpration, Kyoto, Japan), with the metal side and polymer side clamped parallel to the tension axis so that a shear force acted on the bond interface and the maximum load at failure for each of the joints, bonded under the different conditions, was measured at a cross-head speed of 1.66 × 10^{-3} mm/s. The tensile shear strength values were obtained from five specimens for each condition, and the average values are presented in the figures. The untreated PEEK surface without plasma exposure was used as the control.

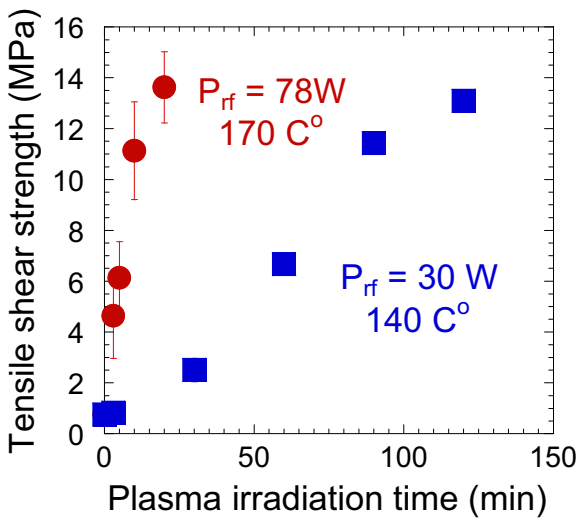

Fig. 2. Tensile shear strength of untreated TP340 and plasma irradiated PEEK samples bonded by hot pressing method as a parameter of RF power.

2.3. Evaluation of physical and chemical state of plasma-treated PEEK surface

The observation of cross-section of the PEEK was carried out by scanning electron microscopy (SEM; SU-70, Hitachi Ltd., Tokyo, Japan). The results shown in this section are representative of repeated measurements under each condition. The reproducibility of the observations was confirmed. The etching depth of the PEEK was measured with a stylus surface profiler (SURFCOM 1400D, Tokyo Seimitsu, Tokyo, Japan). The difference in height between the plasma-irradiated surface and the non-irradiated surface of the PEEK surface is used as the etching depth, and the etching rate is calculated from the height and plasma irradiation time. The surface morphologies of the PEEK were examined using atomic force spectroscopy (AFM; VN-8000, KEYENCE, Osaka, Japan). All AFM images in this study were acquired from regions 50 × 50 μm in size. The chemical bonding state of the nanoscopic layer on each plasma-exposed polymer surface was analyzed using X-ray photoelectron spectroscopy (XPS; AXIS165, Simadzu Corpration, Kyoto, Japan).

2.4. Evaluation of biocompatibility of plasma-treated PEEK

Prior to in vitro evaluation, all samples were sterilized in 70 % ethanol and then thoroughly rinsed with deionized water. MC3T3-E1 cells (RIKEN BioResource Center, Ibaraki, Japan), a commonly used osteoblast-like cell line, were cultured in an alpha modification of Eagle's minimum essential medium (MEMα; FUJIFILM Wako Pure Chemical, Osaka, Japan) supplemented with 10 % fetal bovine serum (HyClone; Cytiva, Marlborough, MA, USA), 100 U/mL penicillin, 100 μg/mL streptomycin, and 0.25 μg/mL amphotericin B (FUJIFILM Wako). These cells were maintained at 37 °C in a humidified atmosphere containing 5 % CO_2. After incubation, the cell suspension was diluted to obtain concentrations of 1.0 × 10^4 cells/mL and 1 mL of the cell suspensions was seeded onto each sample. After 6 h of incubation, the cell suspension was removed to eliminate non-adherent cells, and the medium was replaced with fresh medium. The number of viable cells on each sample surface after 6, 24, 72, and 120 h of incubation was determined using a water-soluble tetrazolium salt (Cell Counting Kit-8 [CCK-8]; DOJINDO, Kumamoto, Japan) (n = 8). Statistical analysis was performed using Student's *t*-test with KaleidaGraph software (version 4.1.1; Synergy Software, Eden Prairie, MN, USA). A *p*-value of <

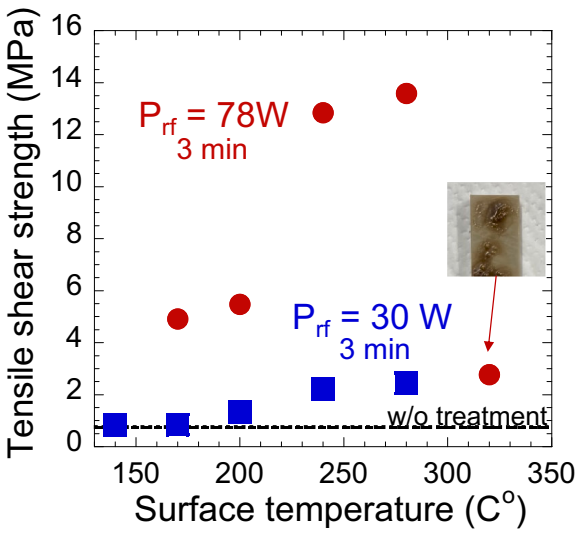

Fig. 3. Surface temperature dependence of tensile shear strength of untreated TP340 and plasma irradiated PEEK samples as a parameter of RF power.

0.05 was considered statistically significant in this study.

3. Results and discussion

First, PEEK specimens irradiated with different plasma generation conditions were directly bonded to TP340 by a hot-pressing method. Plasmas generated at RF power 78 W and 30 W were irradiated only to PEEK specimens. Fig. 2 shows the variation of the tensile shear strength of samples bonded by hot pressing as a parameter of plasma irradiation time. In both conditions, the bond strength tended to increase linearly with increasing irradiation time, and the bond strength was 13~14 MPa. On the other hand, the irradiation time to obtain the same bonding strength was one-sixth longer when the plasma generated at 30 W was irradiated than when the plasma was generated at 78 W, which is a lower RF power. Since the surface is heated by the heat flux from the plasma when the plasma is irradiated, the surface temperature was observed under each plasma irradiation condition, and it was found that the surface temperature increased by 170 °C for 78 W and 140 °C for 30 W during plasma irradiation. First, to investigate the effect of temperature, the dependence of bond strength on surface temperature during plasma irradiation was examined for 78 W and 30 W irradiation. When the surface temperature was above the temperature raised by the heat input from plasma irradiation, the surface was heated with a heater to achieve the desired surface temperature. Fig. 3 shows the surface temperature dependence of the tensile shear strength of TP340-PEEK direct bonded samples as a parameter of RF power. In the case of 30 W RF power, the increase in bonding strength was gradual as the surface temperature increased, whereas in the case of 78 W RF power, the strength increased dramatically as the surface temperature exceeded 240 °C. Therefore, XPS analysis was performed to investigate the chemical bonding state of the surface concerning bonding strength. Fig. 4 shows the XPS C1s spectra of the surface of (a) pristine PEEK and (b) PEEK treated with 78 W of RF power unheated and heated to 240 °C by a heater, respectively. In pristine PEEK, the XPS C 1 s spectra exhibits no discernible changes with and without heating, with peak positions and intensities remaining consistent with the characteristic chemical structure of PEEK [37]. These results indicate that thermal treatment does not induce discernible structural modifications on the PEEK surface.

The effect of plasma irradiation was verified through XPS analysis. Comparison of the XPS spectra of PEEK surfaces treated with 78 W RF

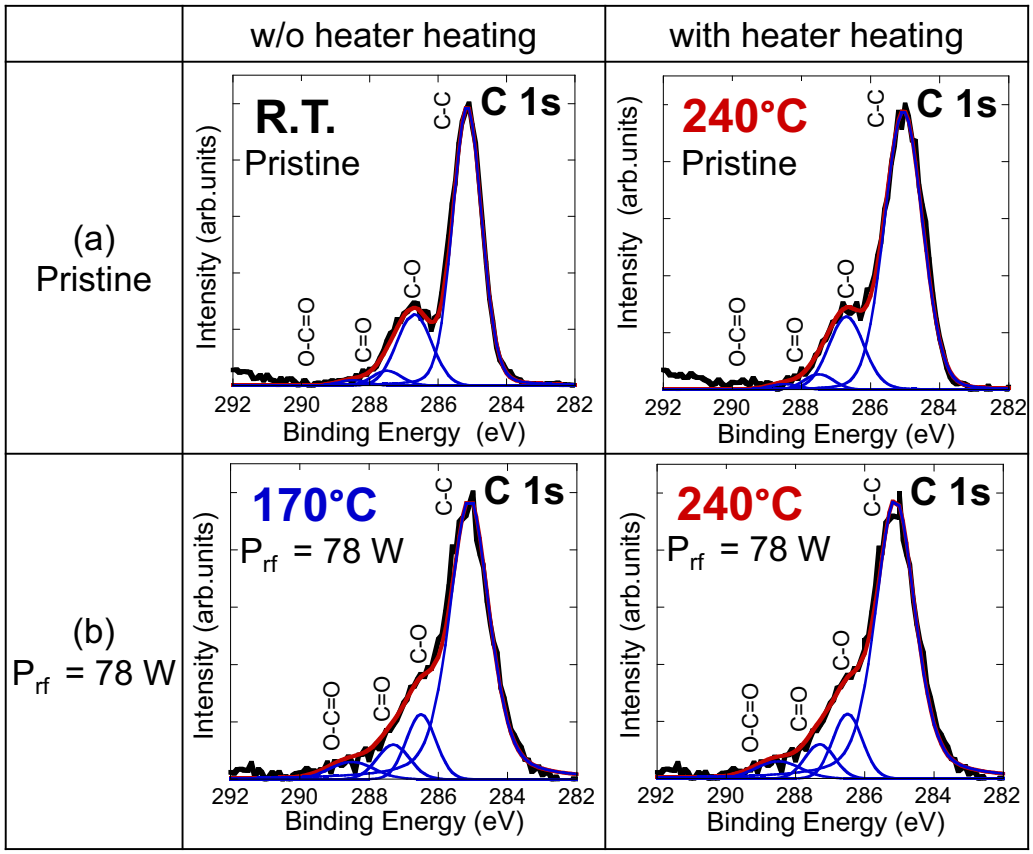

Fig. 4. C 1 s XPS spectra of PEEK surface without and with heater heating as a parameter of RF power.

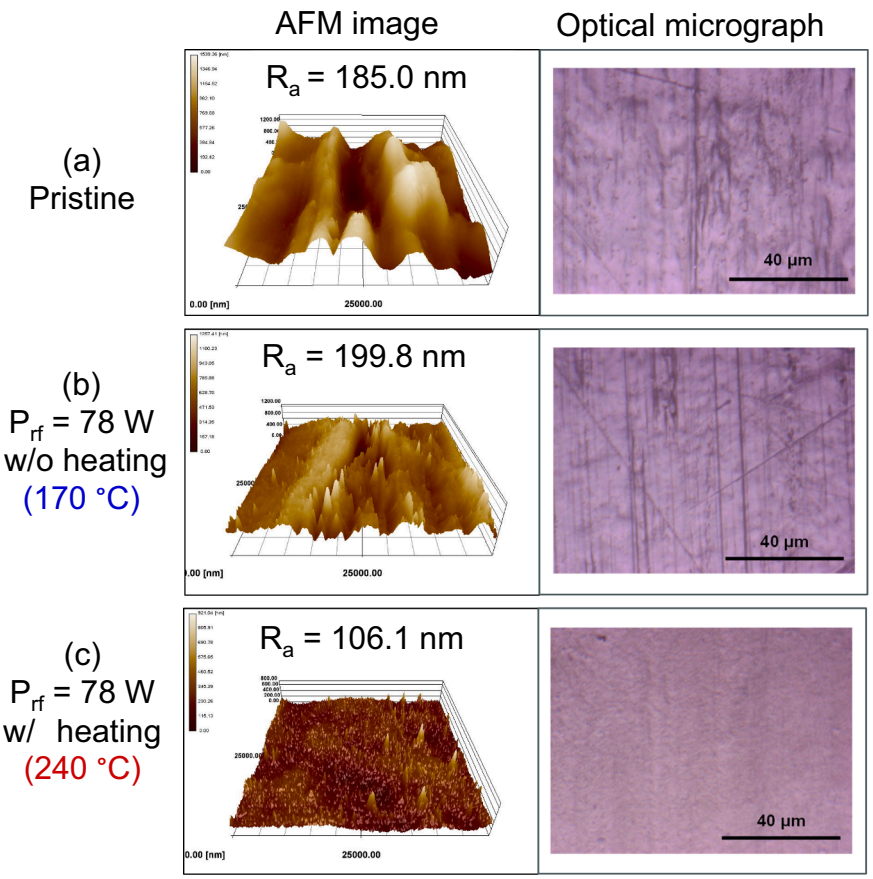

Fig. 5. Variation of surface roughness Ra of PEEK on surface temperature during plasma irradiation.

power without heater heating and those of pristine surfaces revealed the emergence of O–C=O groups, attributable to oxidation, following surface treatment. These results suggest that the atmospheric-pressure plasma irradiation can effectively introduce functional groups onto the PEEK surface, and that such incorporation contributes to the enhancement of bond strength of direct joints. To evaluate the influence of PEEK surface temperature during plasma irradiation on functional group incorporation, XPS spectra of PEEK surfaces treated at 170 °C and 240 °C were compared, revealing that their spectral profiles were nearly identical. This result indicates that variations in surface temperature during plasma irradiation do not significantly affect the introduction of functional groups onto the PEEK surface. In general, O–C=O groups formed on polymers are known to increase the bond strength between metal and polymer following direct bonding [38–40]. From the XPS results for plasma-irradiated PEEK at different surface temperatures, the observation that functional group formation remains unaffected by surface temperature suggests that variations in bonding strength resulting from differences in PEEK surface temperature are attributable to factors other than the chemical bonding state of the PEEK surface. Therefore, to investigate the physical effects of the surface, the surface morphology of the PEEK surface was observed using AFM. Fig. 5 shows the 3D AFM images of (a) pristine, (b) plasma-treated PEEK without heating, and (c) with heating, together with optical micrographs. The surface roughness R_a of the pristine and non-heating PEEK is 185.0 and 199.8 nm, while that of heating PEEK drastically decreased to 106.1 nm. Therefore, cross-sectional SEM images of the surface on (a) pristine PEEK and (b) PEEK that were plasma-irradiated while the substrate was heated were observed. As shown in Fig. 6, the typical SEM image of surface on pristine PEEK showed cracks and voids, which are generally referred to as “weak bonded layers”, were observed from the top surface to about 5 μm in depth. In general, the formation of a weak bonded layers on PEEK arises from rapid surface quenching during the molding process, which suppresses crystallization at the surface relative to the bulk. Consequently, an amorphous, mechanically inferior layer characterized by heterogeneous molecular chain orientation and density is produced. The SEM analysis of pristine PEEK indicates the presence of such surface layers. On the other hand, the plasma-irradiated PEEK surface shows no cracks or voids in the surface layer, and the same structure as the bulk can be seen all the way to the surface. This is considered to mean that the “weakly bonded layers” have been removed by plasma irradiation. The results are presented through post-fracture photographs of bonded specimens exhibiting bond strengths below 5 MPa, which were directly bonded using PEEK treated under conditions that retained a weak boundary layer on the PEEK surface (P_{rf} = 78 W, 3 min, surface temperature: 170 °C in Fig. 3), along with SEM observations of the fracture surface on the Ti side and elemental analysis using SEM-EDX as shown in Fig 7. Although PEEK residues were not discernible by visual inspection, SEM revealed fine residues, several micrometers in size, on the Ti surface. Elemental composition analysis further confirmed that these residues consisted primarily of carbon. These findings suggest that the failure did not occur at the interface itself, but rather through the aggregation and rupture of a fragile surface layer several micrometers thick, resulting in reduced shear strength.

Therefore, the etching depth of PEEK under different plasma irradiation conditions and surface temperatures was investigated. Fig. 8 shows the results of the etching depth of the PEEK surface under different processing conditions as a function of plasma irradiation time. It was found that etching depth increased in a short time as RF power and surface temperature increased, and etching rate increased from 0.02 μm/min at 30 W RF power without heating, to 0.21 μm/min at 78 W RF power without heating and then to 3.74 μm/min with 78 W RF power with heating. In terms of the removal of the weak-bonded layer, the

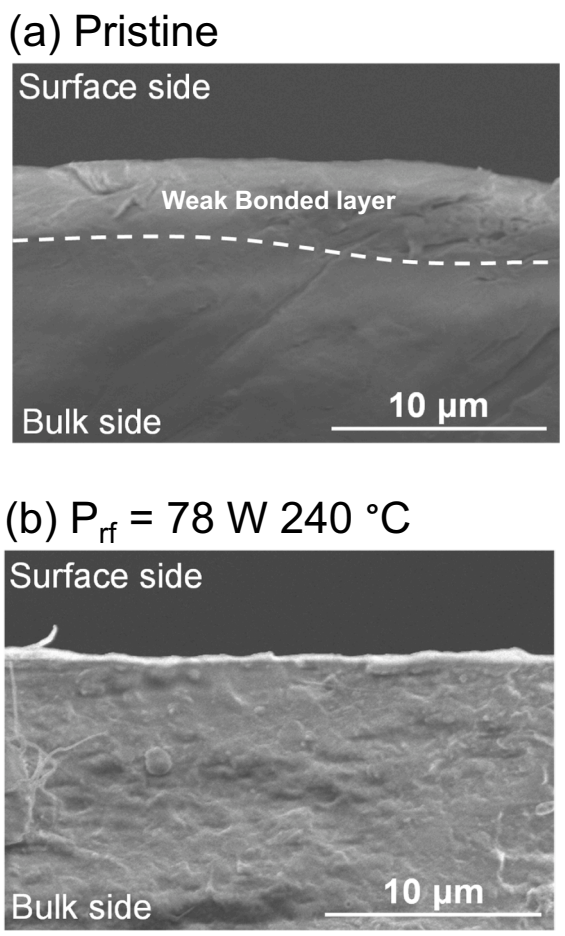

Fig. 6. Cross sectional SEM images of pristine PEEK and plasma irradiated PEEK at surface temperature 240 C.

results of the change in bond strength versus etching depth are shown in Fig. 9. The bond strength increased almost linearly with etching depth from the surface and showed similar bond strength with respect to etching depth for all treatment conditions. In other words, the results show that bonding strength depends on the depth of PEEK etched from the surface, not on the plasma irradiation conditions. The results of this study clearly demonstrate that the weak bonded layer on the PEEK surface is the primary factor responsible for reduced bonding strength, and that complete removal of this weak bonded layer significantly enhances bonding performance. It is well established that a weak bonded layer extends to a depth of several micrometers from the surface, and that sufficient removal via plasma irradiation can effectively improve bonding strength. These results suggest that plasma treatment is effective not only in imparting functional groups but also in eliminating structurally weak bonding layers, with these effects acting synergistically to produce enhanced bonding strength.

Furthermore, the MC3T3-E1 cells were seeded and cultured on pristine PEEK and PEEK treated with 78 W of RF power to investigate biological performance. The PEEK utilized in this investigation of biological performance was subjected to plasma treatment under conditions optimized to effectively introduce functional groups onto the surface (P_{rf} = 78 W, 5 min, surface temperature: 170 °C).

Fig. 10 shows the values of optical density at 450 nm (OD_{450}) in each sample after 6, 24, 72, and 120 h of incubation. In this study, since viable cells were measured using the CCK-8 assay, the OD_{450} values reflects the number of viable cells. The OD_{450} value in PEEK treated with 78 W of RF power after 6 h of incubation was significantly higher than that in pristine PEEK, indicating that more MC3T3-E1 cells adhered to the

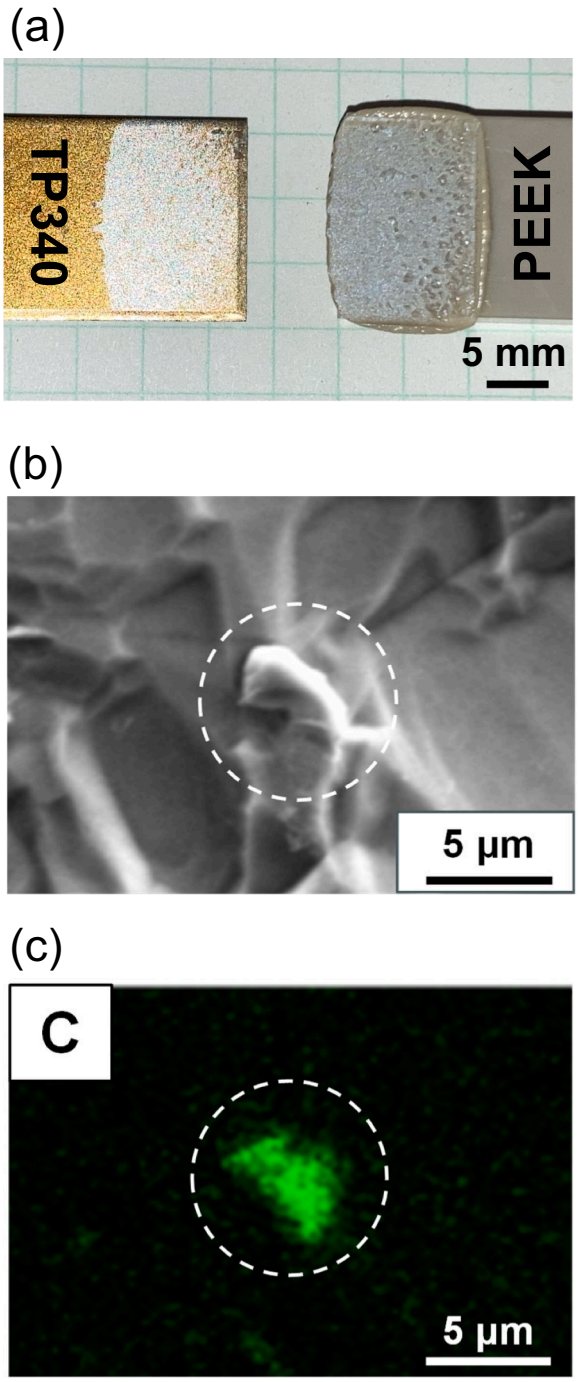

Fig. 7. Photographic images of fracture surfaces after tensile testing of specimens (a); SEM images (b); and SEM–EDX elemental maps of carbon (C, shown in green) (c) on the fracture surface of TP340.

plasma-treated PEEK surface. In general, events at the bone–implant interface are initiated from the protein adsorption, subsequently cellular adhesion and proliferation, and ultimately result in bone tissue formation [41]. Moreover, surface characteristics of implant materials critically govern cellular responses. Among these characteristics, the polar functional groups exhibiting hydrophilicity, such as O–C=O groups, improve the cellular adhesion and proliferation by promoting the adsorption of adhesive proteins [42,43]. In this study, the O–C=O groups were detected only from the plasma-treated PEEK due to surface oxidation (Fig. 4). Therefore, it is considered that the PEEK treated with 78 W of RF power improved cellular adhesion thorough promoting

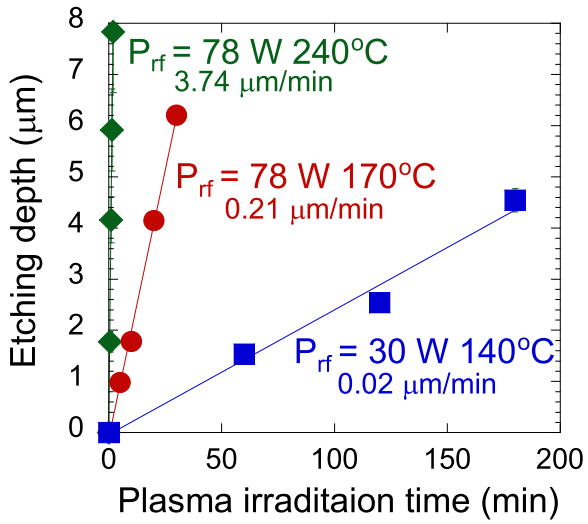

Fig. 8. Etching depth of PEEK surface under different processing conditions as a function of plasma irradiation time.

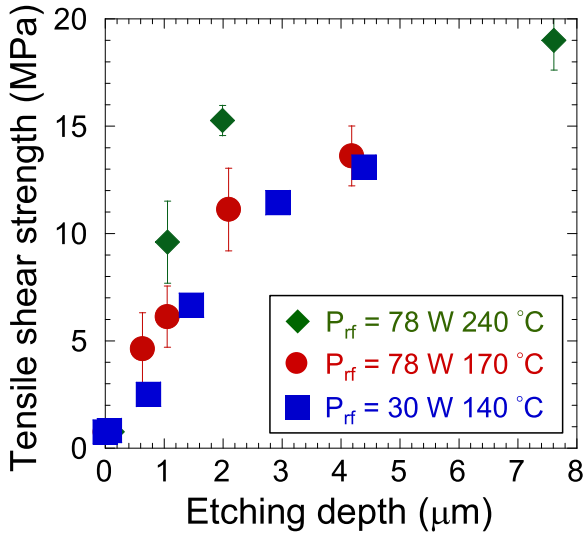

Fig. 9. Variation of tensile shear strength of bonded samples using untreated TP340 and plasma-irradiated PEEK versus etching depth of PEEK surface.

adhesive protein absorption via the O–C=O groups on the surface. Furthermore, the OD_{450} values in PEEK treated with 78 W of RF power after 24, 72, and 120 h of incubation were significantly higher than those in pristine PEEK. Therefore, the cellular proliferation of MC3T3-E1 cells was promoted on the PEEK surface treated with 78 W of RF power. Similar to cellular adhesion, surface characteristics of implant materials also influence the proliferation of osteoblasts [44]. Since anchorage-dependent cells such as osteoblasts will not divide without prior stretching on the material surfaces [45], it is considered that MC3T3-E1 cells attached and spread more effectively on plasma-treated PEEK than on pristine PEEK, thereby demonstrating favorable proliferation behavior. Therefore, plasma treatment endowed the PEEK surface with improved biological performance, highlighting its advantages as a surface modification for PEEK-based implant materials. Zheng *et al.* also reported that plasma treatment forming the O–C=O groups to PEEK surface promoted the cellular adhesion and proliferation of pre-osteoblasts [43]. However, they further demonstrated that although the spreading of pre-osteoblasts improved with increasing O–C=O surface content, cellular adhesion and proliferation were reduced.

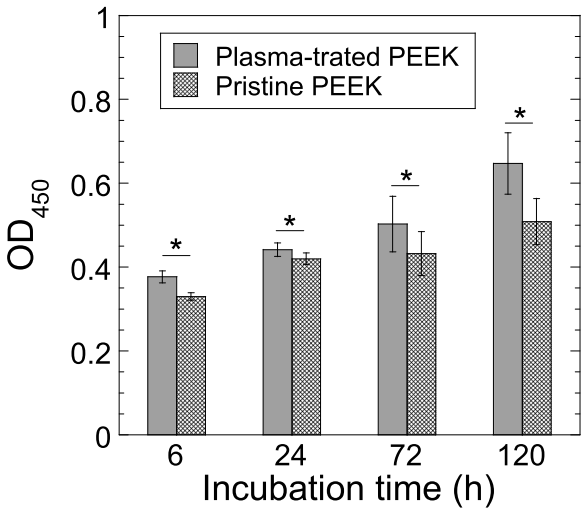

Fig. 10. Cell adhesion and proliferation of MC3T3-E1 cells cultured on different PEEK surfaces over a period of 6 to 120 h. Data are shown as the mean ± SD. "*" denotes significant differences between the indicated samples ($p < 0.05$).

Therefore, further studies are required to determine the optimal surface content of O–C=O groups that favor osteoblast adhesion, spreading, and proliferation. In the present study, we demonstrated that the plasma treatment enhanced MC3T3-E1 cells adhesion and proliferation on PEEK surfaces due to the formation of O–C=O groups. These findings suggest that this technique may promote osteogenesis on PEEK, thereby contributing to improved initial fixation and long-term stability of PEEK implants.

4. Conclusions

The effect of plasma irradiation on PEEK on the physical and chemical state of the PEEK surface was investigated in terms of bond strength in PEEK-metal direct bonding. PEEK treated with atmospheric pressure plasma jets with sustained RF power and untreated TP340 were joined using a hot-pressing method. The bonding strength was evaluated by focusing on the plasma irradiation conditions. The bonding strength tended to increase linearly with increasing irradiation time, and finally reached about 14 MPa under all irradiation conditions. To investigate the effect of the bonding strength on the surface temperature during plasma irradiation, the bonding strength of PEEK with the surface temperature as a parameter was investigated under different plasma irradiation conditions. Therefore, XPS analysis was performed to investigate the chemical bonding state of the surface with respect to bond strength. The XPS C1s spectra of the PEEK treated with 78 W of RF power at surface temperature 170 °C to 240 °C show the O–C=O group attributed to surface oxidation, and the spectral shapes are almost identical. This result suggests that the increase in bond strength at different surface temperatures is due to other factors than the chemical bonding state of the PEEK surface. Therefore, to investigate the physical effects on the surface, the morphology of the PEEK surface using AFM and SEM was observed. The cracks and voids, generally called "weak bonding layers" seen on the pristine PEEK surface were not confirmed on the surface layer of the plasma-irradiated PEEK surface. When evaluated by the bond strength against the etching depth by plasma irradiation, the bond strength increased almost linearly with the etching depth from the surface and in all plasma conditions, the bond strength corresponded to the etching depth. This result indicates that the weak bonding layer on the surface affects the bond strength, and that the complete removal of the weak bonding layer clearly indicates that the bond strength is improved. Furthermore, the biological performance of the plasma-irradiated PEEK surface was investigated using MC3T3-E1 cells. The

cells adhered and proliferated more effectively on the plasma-irradiated PEEK surface, owing to the presence of O–C=O functional groups.

CRediT authorship contribution statement

Kosuke Takenaka: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Soutaro Nakamoto:** Investigation, Formal analysis. **Masaya Shimabukuro:** Methodology, Investigation, Formal analysis, Conceptualization. **Akiya Jinda:** Investigation, Formal analysis. **Ryosuke Koyari:** Investigation, Formal analysis. **Shunsho Shigemori:** Investigation, Formal analysis. **Kouki Ueno:** Investigation, Formal analysis. **Susumu Toko:** Investigation, Formal analysis. **Giichiro Uchida:** Supervision, Methodology, Conceptualization. **Masakazu Kawashita:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization. **Yuichi Setsuhara:** Writing – review & editing, Supervision, Project administration, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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