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RESEARCH AND EDUCATION

Diazonium chemistry for bonding between PEEK and resin cement

Saadet Atsu, DDS, PhD,[a] Ahmed Saad, BEng, MSc,[b] Faleh Tamimi, BDS, MSc, PhD,[c] and Marta Cerruti, PhD[d]

ABSTRACT

Statement of problem. Polyetheretherketone (PEEK) is an excellent restorative material, but its hydrophobicity and inertness prevent strong adhesion to resin cements.

Purpose. The purpose of this in vitro study was to examine the use of diazonium reactions for priming PEEK surfaces to improve their adhesion to resin cements.

Material and methods. Polished PEEK specimens were exposed to 7 different treatments: airborne-particle abrasion (50 μm) (APA), diazonium priming (D), adhesive (visio-link) application (A), APA followed by A (APAA), D and A (DA), APA and D (APAD), and APA followed by D and A (APADA). Nontreated specimens served as controls (C). The surface composition, roughness (Ra), and contact angle of the specimens were examined before and after treatment using X-ray photoelectron spectroscopy (XPS), profilometry, and goniometry respectively. The tensile bond strength between the treated specimens and resin cement (Panavia SA) was evaluated with a mechanical testing machine after incubation in distilled water (24 hours, at 37 °C). The fracture surfaces were examined by using a stereomicroscope at ×40 magnification. The Kruskal-Wallis, 1-way analysis of variance, Tukey HSD, and Fisher-Freeman-Halton tests were used for statistical analysis (α=.05).

Results. Surface characterization revealed that the APA treatment resulted in the highest surface concentration of oxygen and the highest contact angle (81.3 ±4.9 degree), the D treatment resulted in the highest surface concentration of nitrogen, the DA treatment resulted in the lowest roughness and contact angle (49 ±6.2 degree), and the APAD treatment resulted in the highest roughness. Tensile test results showed the lowest tensile bond strength in the control group (0.1 ±0.1 MPa) and the highest in the APADA group (13.9 ±1.6 MPa) (P<.001). Differences were not observed among the APAA (10.8 ±0.9 MPa), DA (10.4 ±1.6 MPa), and APAD (9.8 ±1.7 MPa) treatments (P>.05). The failures of the groups were different (P<.05), with group C showing 100% adhesive failure and the APADA group showing 70% mixed failure.

Conclusions. The surface treatment of PEEK with a diazonium primer increased the bonding strength of resin cement to PEEK. (J Prosthet Dent 2025;133:1360.e1-e9)

Polyetheretherketone (PEEK) is a thermoplastic, methacrylate-free, high-performance polymer which is composed of functional ether and ketone groups and aromatic benzene molecules.[1] Its mechanical properties, biocompatibility, chemical resistance, elastic modulus, light weight, radiolucency, and low cost offer advantages in many dental applications.[2–6] PEEK can be easily processed by milling or 3D printing to fabricate a wide range of dental prosthetic components, including implant abutments, prosthesis frameworks, and fixed and removable partial dentures.[2–7] However there are some limitations to its clinical use.[2,3] Its opacity compromises esthetics, and it often needs to be veneered with more esthetic materials such as resins or ceramics when used for fixed prostheses.[4–7] Moreover, its adhesion to polymethylmethacrylate (PMMA), ceramics, and resin is low because of its inert chemical nature.[2,3] Therefore, surface modifications are necessary for bonding,[1–3,7–13] with different surface modifications being proposed to improve PEEK bonding,[2–4,8–17] including acid etching,

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[a]Visiting Professor, Department of Mining and Materials Engineering, Faculty of Dental Medicine and Oral Health Sciences, McGill University, Montreal, Quebec, Canada; and Professor, Department of Prosthodontics, Faculty of Dentistry, University of Kırıkkale, Kırıkkale, Turkey.
[b]Researcher, Department of Mining and Materials Engineering, McGill University, Montreal, Quebec, Canada.
[c]Professor, College of Dental Medicine, QU Health, Qatar University, Doha, Qatar.
[d]Professor, Department of Mining and Materials Engineering, McGill University, Montreal, Quebec, Canada.

Clinical Implications

PEEK pretreatment with diazonium primers in combination with airborne-particle abrasion and MMA adhesives may enhance PEEK bonding to resin cement.

airborne-particle abrasion, silica coatings, and adhesive treatments.[2,3,8–17] However, none of these strategies have been able to fully address the problem. Sulfuric acid etching showed the highest bond strength between resin cement and PEEK compared with other surface treatment methods.[2,3] However, the hazardous nature of this chemical limits its application,[2,3,8,9,11] while the other methods are not able to achieve sufficient bonding.[2–7,17–19]

Diazonium molecules act as a coupling agent with chemical bonding capacity.[20–23] Aryldiazonium salts can bind to the surfaces of various materials such as metals, carbon-based materials, and polymers.[20–25] Diazonium radicals are obtained by reducing aromatic amines into diazonium ions first and then stable radicals that can quickly form covalent bonds on different surfaces.[20–25] Diazonium ions can be expressed through the general representation: $R–N_2^+X^-$, where R is an aryl group and X is an organic or inorganic anion. Diazonium compounds can be reduced to radical for covalent binding to surfaces through electrochemical, photochemical, ultrasonic, or chemical methods,[23–25] with chemical application being preferred because of its simplicity.[20–25] In this method, a reducing agent converts aryldiazonium ions to surface-oriented aryl free radicals that are covalently bound to that surface. The result is a surface layer that is solvent resistant and electrochemically and mechanically stable.[23–25] In dentistry, diazonium chemistry has been used for the chemical bonding of metal alloys with composite resin and PMMA, achieving significant improvements in the bond strength.[20–22]

Since the bond strength of resin cement to PEEK is still challenging, the purpose of the present in vitro study was to test the effect of a new surface modification on PEEK using diazonium chemistry for PEEK–resin cement bonding. The null hypothesis was that diazonium chemistry would have no effect on PEEK and resin cement bonding.

MATERIAL AND METHODS

The total number of specimens required was 272, based on 95% power (1-β err probe), 0.29 effect size (f), and α=.05 according to the power analysis (G*Power 3.1; Heinrich Heine University). PEEK specimens were prepared in the form of disks for the evaluation of surface elementary composition (n=2), surface topography (n=2), roughness (n=10), and wettability (n=10) and in the form of rectangular monoliths for the tensile bond strength test (n=20 per group). The disks (Ø12.5×2 mm) were prepared by cutting PEEK rods (McMaster-Carr) while the rectangular monolithic specimens (25×5×3 mm) were cut from a PEEK plate (McMaster-Carr). All specimens were polished under water with silicon carbide paper (800–1200 grit) and cleaned in an ultrasonic cleaner using ethanol and deionized water for 15 minutes each. The specimens were distributed into 8 groups by applying the procedures stated in Table 1. In the APA treatment, 50-μm Al_2O_3 particles (Korox; BEGO) abraded PEEK surfaces at a pressure of 0.2 MPa from a distance of 10 mm for 20 seconds[2,3,8,11] Compressed air was then applied to remove the excess Al_2O_3 particles. Finally, the specimens were cleaned ultrasonically in ethanol and deionized water for 10 minutes.

Table 1. Surface treatments and abbreviations of groups

Surface Treatments	Abbreviations
Airborne-particle abrasion	APA
Diazonium priming	D
Adhesive application	A
Airborne-particle abrasion followed by adhesive	APAA
Diazonium priming and adhesive	DA
Airborne-particle abrasion and diazonium priming	APAD
Airborne-particle abrasion followed by diazonium priming and adhesive	APADA
Non-treated controls	C

For the diazonium treatment (D), PEEK specimens were first added to a solution of p-phenylenediamine (540 mg, 5 mmol) (Sigma-Aldrich) in (1 M) hydrochloric acid (25 mL, 25 mmol) (Sigma-Aldrich) and then cooled to 5 °C in an ice bath.[21–23] Then, a cold solution of sodium nitrite ($NaNO_2$) (Sigma-Aldrich) (345 mg, 5 mmol/25 mL DW) (5 °C) was added drop wise to the p-phenylenediamine solution, resulting in a brownish-red color indicative of the formation of diazonium salts, and was mixed for 5 minute to obtain diazonium radicals. Hydrochloric acid (2.75 mL, 25 mmol) was then added under constant stirring (500 rpm) for 2 hours at room temperature (Fig. 1). At the end of the reaction, the PEEK specimens were removed, washed and sonicated in deionized water for 15 minutes, and dried with compressed air.[21–23]

For the adhesive treatment (A), a thin uniform layer of adhesive (Viso.link; bredent group GmbH Co KG) containing dimethacrylate, methylmethacrylate (MMA) and pentaerythritol triacrylate (PETIA) was applied for 1 minute and light polymerized using a dental polymerization device (220 mW/cm^2) for 90 seconds. For the airborne-particle abrasion–adhesive treatment (APAA), both the APA and A procedures were applied consecutively. For the diazonium–adhesive treatment (DA), both the D and A procedures were applied consecutively. For the airborne-

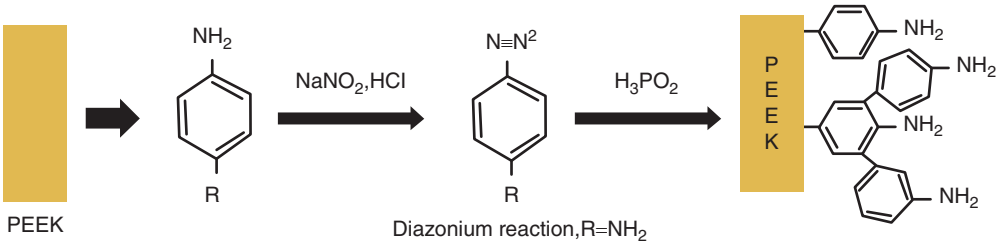

Figure 1. Diazonium modification of PEEK surface with NH_2. PEEK, polyetheretherketone.

particle abrasion—diazonium treatment group (APAD), both the APA and D procedures were applied consecutively. For the airborne-particle abrasion—diazonium—adhesive treatment group (APADA), the APA, D, and A procedures were applied in a subsequent manner.

The surface elementary composition of the specimens was evaluated by X-ray photoelectron spectroscopy (XPS) (ThermoK—alpha; Thermo Fisher Scientific Inc) with an Al Kα X-ray source (1486.6 eV) and a Ø400-μm spot size. Three survey scans (0–1350 eV with a pass energy of 200 eV at steps of 1.0 eV) and a high-resolution scan for carbon (with a pass energy of 50 eV at steps of 0.1 eV) were recorded (n=2). The peak fitting and data analyses were done with a software program (Avantage 5.41v; Thermo Fischer Scientific Inc). Two specimens from each group were 4-nm platinum coated (EM ACE600; Leica Microsystems) and evaluated by scanning electron microscopy (SEM) (FlexSEM 1000 II; Hitachi High—Technologies Corp) with an accelerating voltage of 10 kV at ×550 magnification to observe the surface topography. The specimen roughness (Ra) was assessed by profilometry (Perthometer M2; Mahr Group) with a 4-μm radius tip. Measurements were done on 3 different areas per specimen (n=10). The surface wettability of the specimens (n=10) was evaluated with water contact angle (WCA) by using a goniometer (DSA30; KRÜSS Scientific). Droplets (0.3 μL) of distilled water were added onto the specimen in 2 different areas. Images of the droplets were made by a high-resolution camera and zoom lens, and an image evaluation algorithm of the Advance software program was used.

Two rectangular-shaped specimens were bonded to each other on the treated surfaces using resin cement containing10-methacryloyloxydecyl dihydrogen phosphate (MDP), bisphenol A-glycidyl methacrylate (bis-GMA), triethylene glycol dimethacrylate (TEGDMA), and aromatic dimethacrylates (Panavia SA Cement Universal; Kuraray Noritake Dental Inc). The resin cement was applied to each specimen's bonding area and the specimens were then subjected to a constant load of 50 N on a mechanical test device (UniVert; CellScale). The residual cement was cleaned and light polymerized at 1200 mW/cm^2 (Elipar S10; 3M ESPE) for 80 seconds before incubating the specimens in distilled water for 24 hours at 37 °C. Afterwards, the attached specimens were mounted on a mechanical test device (UniVert; CellScale), and a pull-out force was applied at 1 mm/minute. The bond strength (bs) was computed using the test machine's software program with the formula: bs (MPa)=load at failure (N)/adhesive area (mm^2). Failures were observed with a stereomicroscope (Leica MZ12; Leica Microsystems) at ×40 magnification. Statistical analysis was performed using a software program (SPSS v15.0; SPSS Inc). Normal distribution of data was assessed using the Shapiro-Wilk and Kolmogorov-Smirnov tests. The data were analyzed using the Kruskal-Wallis, 1-way analysis of variance (ANOVA), Tukey HSD, and Fisher-Freeman-Halton tests (α=.05).

RESULTS

The atomic percentages of the surface elemental compositions for the groups are presented in Figure 2A. The surfaces functionalized with diazonium reaction of groups D and APAD resulted in a higher surface concentration of nitrogen (N) (8.7 ±1.2, 95% CI [7.2, 10.1] and 9.6 ±0.3, 95% CI [9.2, 10], respectively) and a lower concentration of oxygen (O) (8.0 ±0.1, 95% CI [7.8, 8.2] and 8.8 ±0.2, 95% CI [8.5, 9], respectively) compared with the airborne-particle abraded (26.2 ±2.9, 95% CI [22.6, 29.8]) and control (13.7 ±1, 95% CI [12.5, 14.9]) surfaces (χ^2(7, n=2)=33.30, P<.001; normality was tested with the Kolmogorov-Smirnov test (D)=0.46, P<.001 for N and χ^2(7, n=2)=33.68, P<.001; D=0.22, P<.001 for O). Groups DA and APADA did not show any N, possibly because the adhesive layer was obscuring the presence of N from the diazonium layer. The XPS general survey spectra of groups C and D are represented in Figure 2B, C. N1s (Fig. 2D, E) and C1s (Fig. 2F-H) high resolution XPS spectra were analyzed to evaluate the nature of the functional groups introduced. C1s high resolution spectra of the control PEEK and APA showed peaks corresponding to C═O, C-O, and C-C bonds at 287.0 eV, 286.3 eV, and 284.8 eV, respectively (Fig. 2F, G). After the diazonium reaction, the C═O peak disappeared, and a broader peak at approximately 286 eV was observed that could be attributed to both of the C-O bonds and the newly introduced C-N bonds (Fig. 2H).

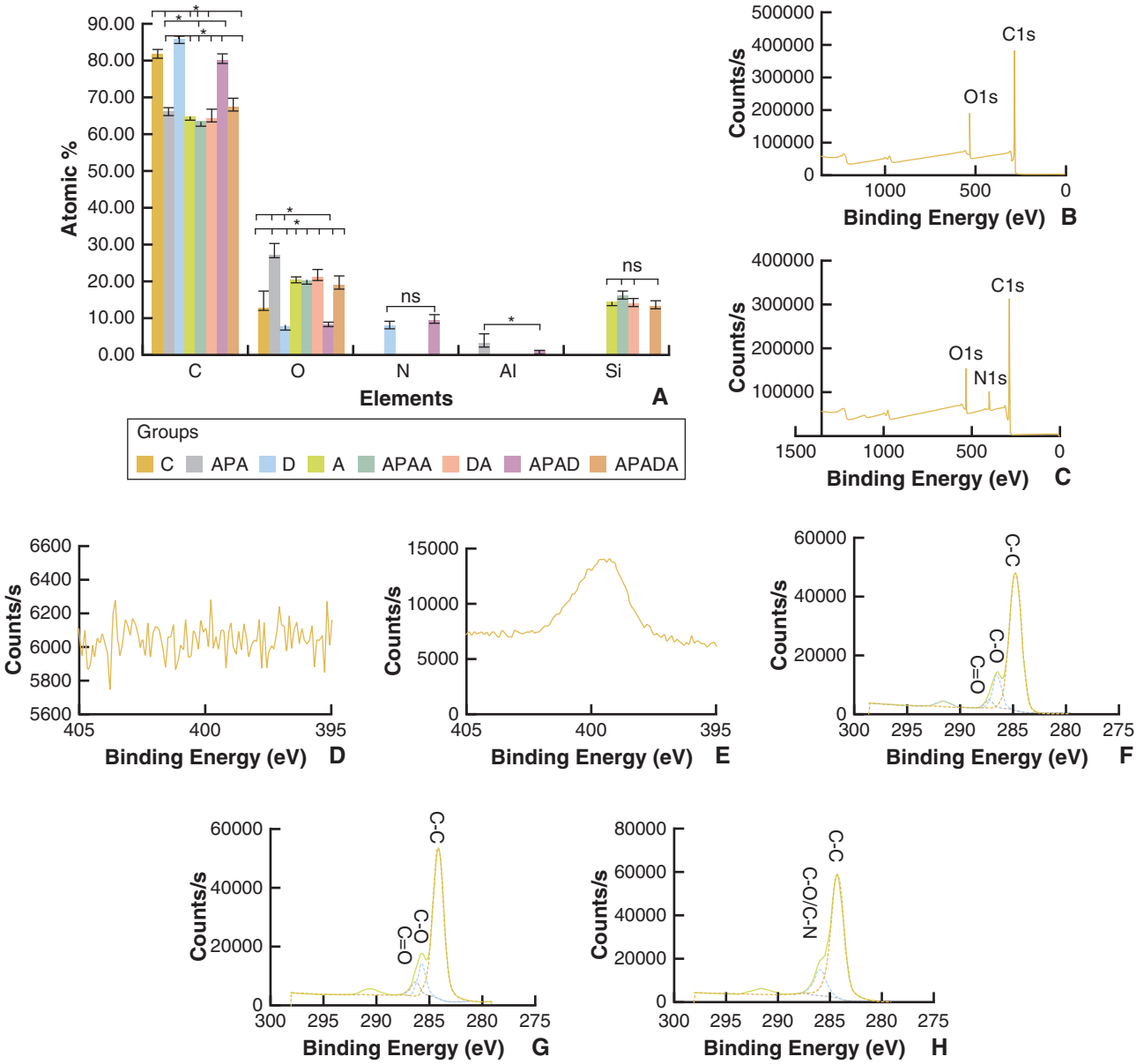

Figure 2. A, Atomic percentage of elements detected on surface of groups based on XPS survey spectra. B, Representative survey spectra of group C. C, Representative survey spectra of group D showing presence of N only. D, Representative high resolution N1s XPS spectra of group C. E, Representative high resolution N1s XPS spectra of group E, confirming presence of N. Peak centered at approximately 399 eV indicative of amino groups on this specimen. C1s XPS spectra of groups C (F), APA (G), and D (H). A, adhesive application; APA, airborne-particle abrasion; APAA, airborne-particle abrasion followed by adhesive; APAD, airborne-particle abrasion and diazonium priming; APADA, airborne-particle abrasion followed by diazonium priming and adhesive; C, control; D, diazonium priming; DA, diazonium priming and adhesive application; ns, non-significant; XPS, X-ray photoelectron spectroscopy. *P<.01.

N1s high resolution spectra also support these findings: there were no peaks in the N1s spectrum of the control PEEK (Fig. 2D), while a centered at 399 eV, indicative of NH_2/–N═N– groups, was clearly visible in the diazonium modified specimens (Fig. 2E). SEM images were obtained at ×550 magnification to observe the surface topography of the groups (Fig. 3A-H). The surface roughness was different among the groups (χ^2(7, n=10) =74.29, P<.001; D=0.15, P<.001) (Fig. 3I). The roughness of the PEEK surface was increased by using airborne-particle abrasion. While group APAD had the highest roughness value (3.8 ±0.2 µm, 95% CI [3.7, 4.0]), group DA had the lowest value (0.21 ±0.1 µm, 95% CI [0.1, 0.3], P<.001). The contact angles of the groups were significantly different (χ^2(7, n=10)=61.31, P<.001; D=0.19, P<.001) (Fig. 4A-I). While the highest WCA was found in group APA (81.3 ±4.9 degree, 95% CI [77.7, 84.8]), the lowest WCA was found in group DA (49 ±6.2

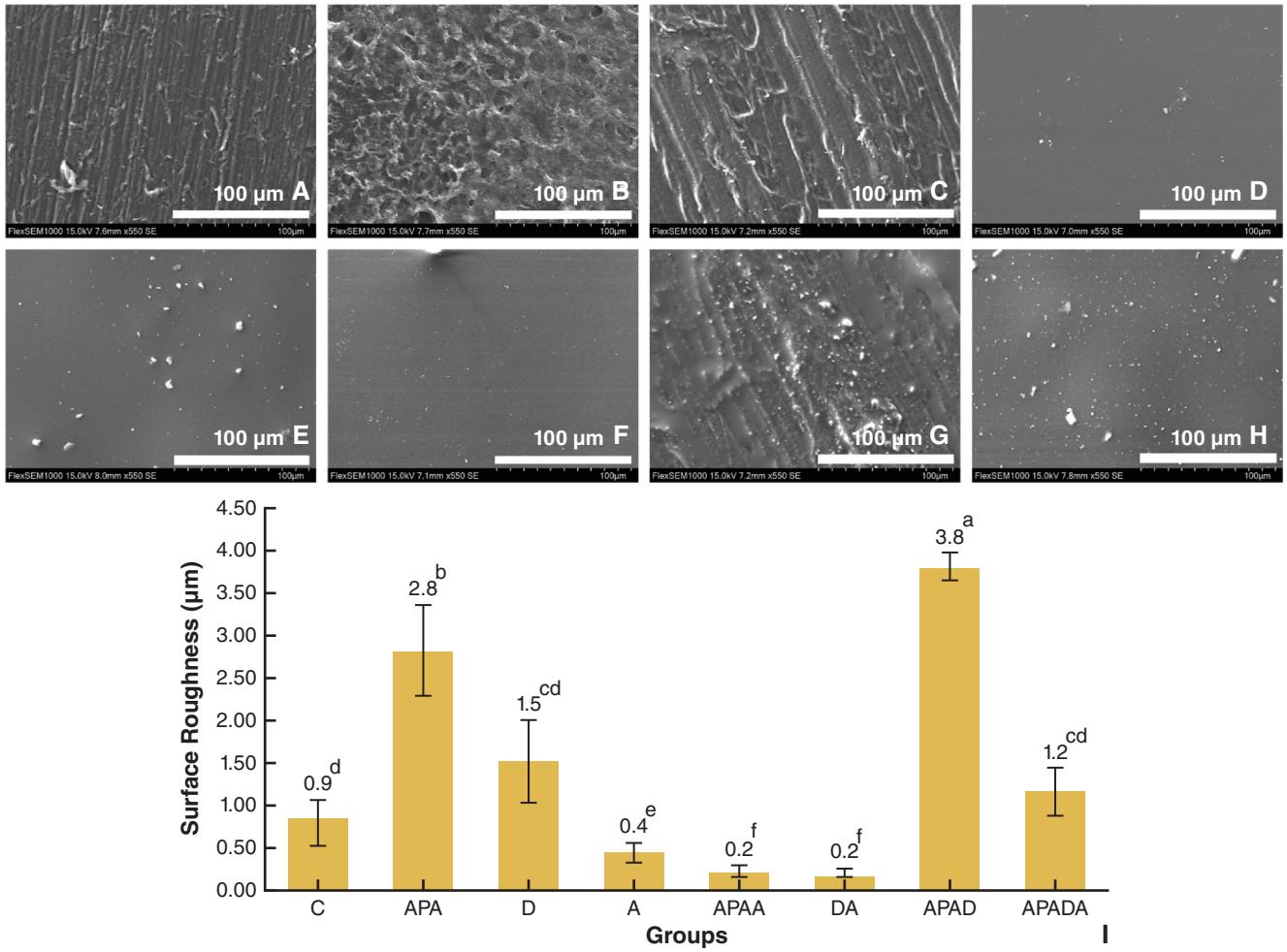

Figure 3. Representative SEM images (original magnification ×550) of surface topographies of groups. A, Control PEEK polished under water with silicon carbide paper showing surface scratches. B, Group APA exhibited concave and convex irregular surface. C, Group D showing surface grooves and scratches. D, Group A showing smooth surface. E, Group APAA exhibited smooth surface. F, Group DA showing smooth and regular surface. G, Group APAD had grooves. H, Group APADA exhibited smooth and regular surface. I, Surface roughness of groups (mean and standard deviation). Different lowercase letters on graph indicate differences (P<.001). A, adhesive application; APA, airborne-particle abrasion; APAA, airborne-particle abrasion followed by adhesive; APAD, airborne-particle abrasion and diazonium priming; APADA, airborne-particle abrasion followed by diazonium priming and adhesive; C, control; D, diazonium priming; DA, diazonium priming and adhesive application; PEEK, polyetheretherketone.

degree, 95% CI [44.6, 53.5], P<.001) (Fig. 4B, F). Representative images of the tensile test experiment are shown in Figure 5A and B. The ANOVA test (F(7, 72) =154.66, P<.001; D=0.86, P=.200) showed that the groups differed in tensile bond strength (Fig. 5C). The highest bond strength was in group APADA (13.9 ±1.6 MPa, 95% CI [12.8, 15.1]), and the lowest bond strength was in group C (0.1 ±0.1 MPa, 95% CI [0.0, 0.2], P<.001). The failure types were significantly different (χ^2(7, n=10) =14.58, P<.05; D=0.35, P<.001) (Fig. 6).

DISCUSSION

Diazonium chemistry significantly increased the bond strength of resin cement to PEEK. Therefore, the null hypothesis that diazonium chemistry would not have any effect on PEEK and resin cement bonding was rejected. The chemical inertness and hydrophobicity of PEEK prevents its bonding to resin-based materials.[1–6] Previous studies indicated that surface modification techniques are required for bonding PEEK with resin cements.[2,3,8,9] In the present study, the diazonium reaction was used to change the surface composition of the PEEK surface and modify it with the NH_2 groups. The XPS analysis of the diazonium priming group confirmed the success of the diazonium reaction through the increase in nitrogen and decrease in oxygen content compared with the control group. Previous studies confirmed that the diazonium chemistry method can be used to attach NH_2 groups to PEEK surfaces.[24,25]

Surface roughness can contribute to micromechanical retention and chemical bonding by increasing the surface

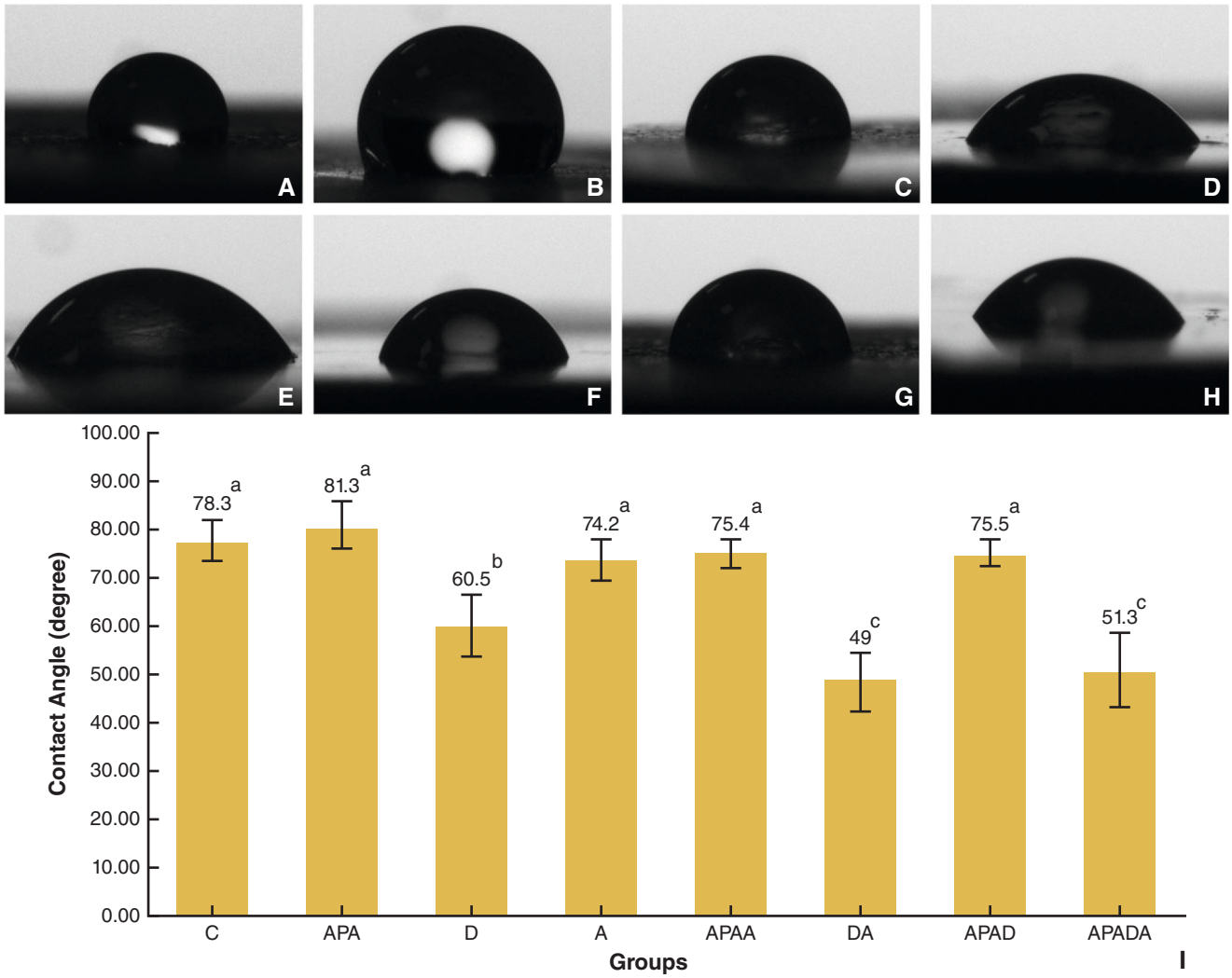

Figure 4. Representative images of water contact angle of groups. A, Group C. B, Group APA. C, Group D. D, Group A. E, Group APAA. F, Group DA. G, Group APAD. H, Group APADA. I, Contact angle means and standard deviation of groups. Different lowercase letters on graph indicate differences (P<.001). A, adhesive application; APA, airborne-particle abrasion; APAA, airborne-particle abrasion followed by adhesive; APAD, airborne-particle abrasion and diazonium priming; APADA, airborne-particle abrasion followed by diazonium priming and adhesive; C, control; D, diazonium priming; DA, diazonium priming and adhesive application.

area for PEEK and resin cement bonding.[2,3,11,15,19] In the present study, although diazonium priming slightly increased the surface roughness, significant differences were not observed compared with the control group, although airborne-particle abrasion significantly increased roughness, as reported previously.[2,3,14–17] In the present study, the roughest surface was found in group APA, consistent with previous studies.[2,3]

Surface wettability is another parameter that affects bonding,[2,3] with increased surface wettability being reported to have a positive effect on the bond strength of PEEK.[2,3] In the present study, after diazonium priming, wettability increased compared with groups C, APA, and A. These results were consistent with those of other studies[23,24] that reported that the hydrophilicity of PEEK surfaces increased with the diazonium reaction.

Previous studies[2,3,8,9] indicated that, in the absence of surface modification, the bond strength between PEEK and resin-based materials was low or nonexistent, consistent with the control group in the present study (0.1 ±0.1 MPa). Etching with 98% sulfuric acid has been proposed as a surface treatment for PEEK.[2,3,9] However, sulfuric acid is corrosive, causing severe burns to the skin, eyes, and respiratory tract if inhaled.[2,3,8,9] Therefore, alternative surface treatment methods such as abrasion with airborne Al_2O_3 particles are recommended to create rough, irregular surfaces and enable micromechanical bonding.[2,3,7–9] Previous studies reported a stronger bond for the PEEK–resin cement compared with the control groups when airborne-particle abrasion was used, reaching 5.3 ±0.6, 5.7 ±0.8, and 6.2 ±1.2 MPa.[8,15,16] The present study confirms this

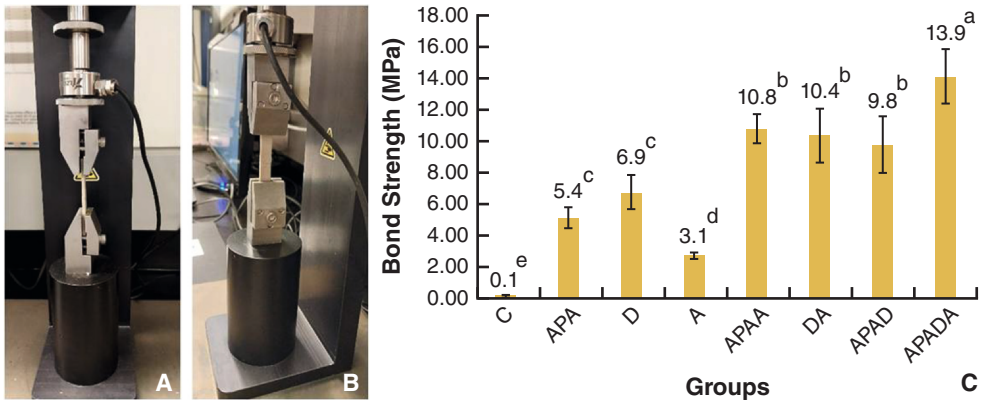

Figure 5. Representative specimens tested with mechanical test device. A, Frontal view of specimen. B, Profile view of specimen. C, Mean and standard deviation of tensile bond strength of groups (MPa). Different lowercase letters on graph indicate differences among groups ($P<.001$). A, adhesive application; APA, airborne-particle abrasion; APAA, airborne-particle abrasion followed by adhesive; APAD, airborne-particle abrasion and diazonium priming; APADA, airborne-particle abrasion followed by diazonium priming and adhesive; C, control; D, diazonium priming; DA, diazonium priming and adhesive application.

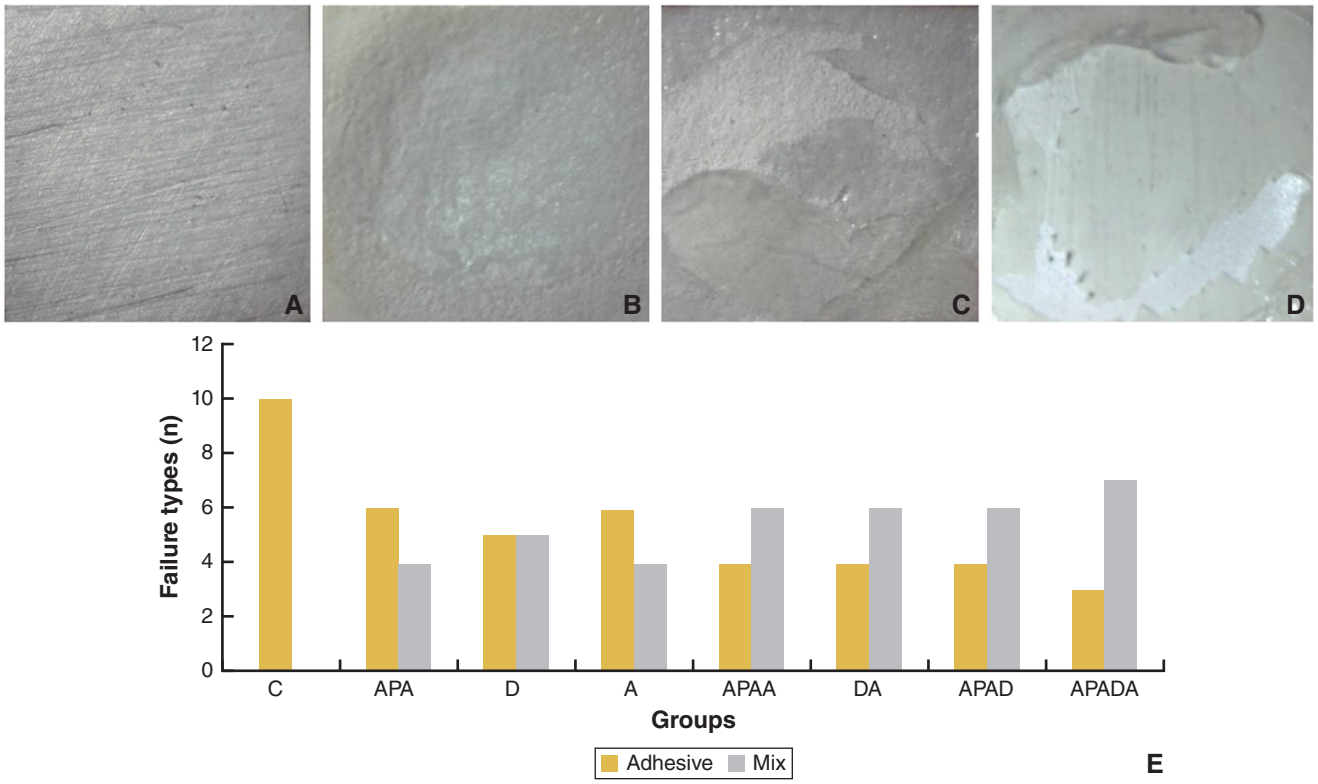

Figure 6. Representative images of failure types of groups. A, Adhesive failure in group C. B, Adhesive failure in group APA. C, Mixed failure in group D. D, Mixed failure of group A. E, Failure types of all groups. A, adhesive application; APA, airborne-particle abrasion; APAA, airborne-particle abrasion followed by adhesive; APAD, airborne-particle abrasion and diazonium priming; APADA, airborne-particle abrasion followed by diazonium priming and adhesive; C, control; D, diazonium priming; DA, diazonium priming and adhesive application.

finding by showing a mean bond strength value of 5.4 ±0.7 MPa when the specimens were abraded with 50-μm airborne Al_2O_3 particles. However, even higher shear bond strength values (6.8 ±1.2, 7 ±4.3, 11.6 ±2.1 MPa) when using 50-μm Al_2O_3 airborne-particle abrasion for reinforced PEEK have been reported.[10,17] This difference may be due to the composition of the PEEK material, type of bond strength test, and resin cement composition.[2,3,10] In the present study, PEEK without inorganic filler was used. A previous study reported that unfilled PEEK had a lower bond strength when bonded to resin material than to filled or reinforced PEEK.[2] A tensile test was used for evaluating bond strength in the present study because it provides a more homogeneous

and uniform stress distribution than a shear test.[12] However, the tensile test tends to lead to lower results than the shear test because of the application of force perpendicular to the bonding area.[2,3,12] In the present study, PEEK bonding to PEEK using a resin cement may not fully reflect clinical practice. However, since the aim of this study was to evaluate only the bond strength between PEEK and resin cement, different materials were not used for bonding.[20]

Different resin cements have been used for PEEK and resin cement bonding.[2,3,17,19] In the present study, resin cement (Panavia SA) composed of MDP and dimethacrylates was used because of the potential chemical bond to PEEK. Micromechanical and chemical surface treatment followed by adhesive application has been recommended to improve bonding and diversify the functional groups of the PEEK polymer.[2,3,7–17] Adhesives that contain MMA showed potential for forming stable chemical bonds between PEEK and resin cement.[2,3,13,14,17] In the present study, using MMA-based adhesive (Visio.link) improved the bond strength of all PEEK groups (P<.001). Group APAA had a higher mean ±standard deviation bond strength (10.8 ±0.9 MPa) than groups APA (5.4 ±0.7 MPa) or A (3.1 ±0.2 MPa) (P<.001). This result was consistent with studies that reported bond strengths of 10.3 ±2.2 MPa and 11.5 ±2.6 MPa for APA followed by adhesive application.[13,18]

Diazonium chemistry has been previously used in 3 studies to increase the bond strength between alloys (titanium and Ni-Cr) and PMMA and composite resin.[20–22] The p-phenylenediamine-based diazotization method was used in these studies, and it was concluded that diazonium coating is a reliable technique to achieve chemical bond between alloys, composite resin, and PMMA.[20–22] In the present study, the p-phenylenediamine-based diazotization method was used, and the treatment of the APADA group showed the highest mean bond strength (13.9 ±1.6 MPa) in all groups (P<.001). Although the highest surface roughness was found in group APAD, no linear relation was observed between the bond strength and increased surface roughness. This result can be interpreted as chemical bonding being more effective than micromechanical bonding for the PEEK−resin cement bond and was consistent with other studies that reported that increasing the surface roughness of PEEK does not always improve the resin cement bond.[2,3] In the present study, it was observed that the combination of diazonium surface modification and adhesive application increases surface wettability and has positive effects on the bond strength, possibly achieving a more reactive surface for bonding. Surface modification with diazonium reactions may also help the binding of the adhesive to PEEK.[10] The authors are unaware of a previous study that investigated the effect of diazonium chemistry on the bond strength of resin-based materials to PEEK. Therefore, the outcome of the present study cannot be compared with other studies. PEEK and diazonium chemistry was investigated in previous studies for osseointegration, biocompatibility, and fibroblast adhesion, and it was concluded that diazonium chemistry improved bioactivity and biocompatibility.[21,23–25] Thus, diazonium priming has advantages compared with other surface modification methods such as sulfuric acid, which has toxic and corrosive risks.

Limitations of the study included the lack of long-term thermocycling and a sulfuric acid surface treatment group and that only 1 type of cement was used. Future research should compare the effects of different diazonium reactions and resin cements on the bond strength of PEEK.

CONCLUSIONS

Based on the findings of this in vitro study, the following conclusions were drawn:

1. Surface modification of PEEK with diazonium reaction increased the bond strength between resin cement and PEEK (P<.001).
2. Diazonium priming increased surface wettability (P<.001).
3. An adhesive containing dimethacrylate, MMA, and PETIA significantly increased the bond strength of resin cement to PEEK (P<.001).
4. Airborne-particle abrasion increased the surface roughness and bond strength (P<.001).
5. Abrasion with airborne Al_2O_3 particles followed by diazonium and adhesive treatment had the highest tensile bond strength among the groups (P<.001).

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Corresponding author:
Dr Saadet Atsu
Faculty of Dentistry
University of Kırıkkale
Yenişehir Mahallesi Çelebi Sokak No:1
Yahşihan/Kırıkkale 71450
TURKEY
Email: saadetats@yahoo.com

CRediT authorship contribution statement

Saadet Atsu: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Visualization, Project administration, Resources, Roles/Writing – original draft, Writing – review and editing. **Ahmed Saad**: Methodology, Validation, Formal analysis, Investigation, Visualization. **Faleh Tamimi**: Methodology, Resources, Writing – review and editing, Supervision. **Marta Cerruti**: Conceptualization, Methodology, Validation, Project administration, Resources, Writing – review and editing, Supervision.

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