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Interfacial Bond Strength of Resin Cement to Polyetheretherketone (PEEK) Using Experimental Primers Doping Multifunctional Methacrylate and Acrylate Monomers

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Abstract

Polyetheretherketone (PEEK) is a high-performance thermoplastic polymer with low surface energy, chemical inertness, and a highly crystalline structure, which limit durable adhesion to resin-based materials and require improved bonding strategies. This in vitro study evaluated the effect of incorporating multifunctional methacrylate (TMPTMA) and acrylate monomers (A-TMPT and A-DPH) into an experimental primer on the 24 h shear bond strength (SBS) of resin cement to PEEK (n = 6 per group). Experimental primers were prepared by adding varying amounts (100–500 μL) of each multifunctional monomer to a UDMA/MMA-based primer, and SBS was measured after cementation with a dual-cure resin cement. TMPTMA-containing primers produced median SBS values of approximately 10–12 MPa, while acrylate-based primers showed slightly higher values, particularly at higher concentrations, reaching up to ~15.8 MPa; however, no statistically significant improvement over the control group was observed ($p > 0.05$). Failure modes were predominantly mixed across all conditions. These findings indicate that multifunctional monomers, despite their potential to enhance cross-link density and wetting, do not substantially overcome the intrinsic adhesion-resistant nature of polished PEEK. The results underscore that monomer modification alone is insufficient and that effective adhesion to PEEK likely requires integrated strategies combining chemical activation with mechanical surface conditioning.

Keywords: PEEK; functional monomer; bond strength; methacrylate; acrylate

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1. Introduction

Polyetheretherketone (PEEK) is a semi-crystalline, high-performance thermoplastic polymer that has garnered substantial interest in restorative and prosthetic dentistry owing to its advantageous mechanical, chemical, and biological characteristics [1,2]. Its elastic

modulus, which approximates that of tooth substrate and cortical bone more closely than metals or zirconia ceramics, facilitates more physiologic stress distribution and enhanced shock absorption. This property reduces the potential for stress shielding and mechanical overloading of abutment structures and peri-implant tissues [3,4]. PEEK has been incorporated into an expanding spectrum of clinical applications, including frameworks for removable and fixed dental prostheses, implant abutments, full-arch implant-supported rehabilitations, and provisional or definitive crowns [5–7]. The material's chemical inertness, high resistance to wear, fatigue, and corrosion, and excellent dimensional stability contribute to its suitability for long-term exposure to the complex oral milieu. Moreover, its low density and radiolucency improve handling characteristics and permit radiographic evaluation with minimal artifact production, distinguishing it from metal-based components [8]. Despite these favorable attributes, PEEK's highly crystalline structure and inherently inert surface present significant obstacles to achieving durable adhesion with resin-based luting agents [6,8]. Insufficient or unstable bonding can impair restoration retention, compromise marginal integrity, and diminish long-term clinical performance, emphasizing the need for more effective adhesion strategies. From a clinical perspective, improving the adhesion of PEEK is essential to ensure long-term retention, marginal integrity, and durability of restorations in load-bearing oral environments. As a result, substantial research efforts have been directed toward improving the bond strength between PEEK and resin cements through mechanical, chemical, and combined conditioning approaches [8–10].

A variety of surface-conditioning techniques have been investigated to enhance the adhesion of resin cements to PEEK. Mechanical treatments—such as airborne-particle abrasion, sandblasting, and controlled surface grinding—are widely employed to modify surface morphology, increase roughness, and promote micromechanical interlocking between PEEK and adhesive materials [11,12]. Although these approaches improve surface texture, they do not sufficiently address PEEK's inherently low surface energy or its lack of reactive functional groups essential for durable chemical bonding [13]. Consequently, several chemical modification strategies have been explored. Plasma treatment and sulfonation have demonstrated the ability to increase surface energy, introduce polar functional groups, and enhance wettability, thereby improving affinity for adhesive resins. In parallel, primers incorporating reactive functional monomers have been developed to promote both chemical interaction and copolymerization with resin cements. Current evidence suggests that integrating mechanical surface roughening with appropriate chemical activation yields synergistic improvements, enhancing early bond strength and potentially supporting long-term interfacial stability under intraoral conditions [14,15]. Nevertheless, the most effective chemical strategy for achieving reliable bonding to PEEK has yet to be established, particularly in relation to primer composition and the strategic use of multifunctional monomers.

Additional chemical approaches investigated for improving PEEK adhesion include oxidative treatments using chromic acid, potassium permanganate, hydrogen peroxide, and piranha solution, all of which can introduce oxygen-containing functional groups and increase surface polarity [14,15]. Various functional monomers and coupling agents, such as 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP), methyl methacrylate (MMA), Bis-GMA, UDMA, TEGDMA, HEMA, and multifunctional acrylates including trimethylolpropane triacrylate (TMPTA) and pentaerythritol tetraacrylate (PETTA), have also been investigated for their potential to improve wettability, interfacial cross-linking, and adhesive durability [16,17]. Although several of these compounds were originally developed for industrial or biomedical polymer applications rather than dental PEEK bonding, their chemical characteristics suggest potential benefits for enhancing resin adhesion to high-performance polymer substrates. Functional monomers constitute critical components

of primer systems formulated for polymeric restorative materials. Methacrylate and acrylate monomers are frequently employed because they can participate in covalent bonding or form strong secondary interactions with resin cement matrices and properly conditioned polymer surfaces [18,19]. Commercial primers commonly rely on monofunctional monomers containing a single polymerizable group; although such monomers can enhance initial adhesion, their limited reactivity may constrain cross-linked network formation, thereby reducing interfacial cohesion and limiting resistance to mechanical and hydrolytic stress. In contrast, multifunctional methacrylate or acrylate monomers—bearing two or more polymerizable groups—may facilitate greater cross-link density, improved wetting of micro-roughened PEEK surfaces, and more uniform stress distribution along the adhesive interface. These benefits are particularly pertinent to the development of reliable early shear bond strength (SBS), which is essential when restorations are subjected to provisional or immediate loading during the first 24 h [20].

Multifunctional methacrylate monomers have been extensively studied for their ability to form highly cross-linked polymer networks and establish robust secondary interactions within resin matrices [21]. Their relatively high reactivity and favorable polymerization kinetics often lead to increased degrees of conversion and improved mechanical performance at the adhesive interface. Furthermore, methacrylate-based polymers exhibit greater resistance to hydrolytic degradation than acrylate-based systems, conferring potential advantages for long-term durability in the moist and thermally dynamic oral environment. Conversely, multifunctional acrylate monomers typically exhibit lower viscosity and faster polymerization kinetics, attributes that enhance penetration into micro-roughened PEEK surfaces and promote superior interfacial wetting [22,23]. These characteristics may facilitate more uniform stress distribution immediately after cementation, improving early retention. However, acrylate-based polymers are generally more susceptible to hydrolytic degradation, which may limit the longevity of the adhesive interface under clinically relevant conditions [24].

Reliable early bond strength is essential for stable cementation at the time of restoration placement, as inadequate adhesion during the initial 24 h period may predispose restorations to early debonding, compromised marginal adaptation, and diminished predictability of clinical outcomes. Strengthening chemical interaction at the PEEK–resin interface may also help counteract the deleterious effects of occlusal loading, thermal cycling, and moisture exposure throughout the service life of the prosthesis, thereby enhancing the long-term clinical performance of PEEK-based restorations. Investigating the incorporation of multifunctional methacrylate or acrylate monomers into experimental primer formulations may therefore provide a scientific basis for improved adhesive strategies for high-performance polymers and expand the clinical utility of PEEK in prosthodontics, implant dentistry, and biomaterials research. Despite these extensive investigations, a key gap remains: current primer systems do not clearly demonstrate whether multifunctional (meth)acrylate monomers alone—without additional aggressive surface modification—can meaningfully improve early adhesion to chemically inert PEEK substrates.

In light of these considerations, the present study was designed to evaluate the effect of an experimental primer containing either a multifunctional methacrylate or a multifunctional acrylate monomer on the SBS of resin cement to PEEK after 24 h of storage. The null hypothesis tested was that the incorporation of these multifunctional monomers into the primer would not significantly influence 1-day SBS compared to untreated PEEK surfaces. This investigation aims to contribute to the refinement of adhesive protocols for PEEK-based dental restorations and to inform future strategies for optimizing both early bond performance and long-term clinical reliability.

2. Materials and Methods

2.1. Preparation of the Base Primer

The base primer was prepared by mixing the following components to a total volume of 1 mL: urethane dimethacrylate (UDMA, 55 wt%), methyl methacrylate (MMA, 15 wt%), and acetone (25 wt%). Camphorquinone (0.4 wt%) was added as a photoinitiator, N,N-dimethylaminoethyl methacrylate (0.8 wt%) was included as a reducing agent, and butylated hydroxytoluene (0.2 wt%) was used as an inhibitor. All components were thoroughly mixed until a homogeneous solution was obtained.

2.2. Preparation of Experimental Surface Treatment Primers

Experimental surface treatment primers were prepared by adding trimethylolpropane trimethacrylate (TMPTMA), trimethylolpropane triacrylate (A-TMPT), or dipentaerythritol hexaacrylate (A-DPH) to the base primer (Figure 1). For each monomer, 100, 200, 300, 400, or 500 μL was added to 1 mL of the base primer, resulting in a series of experimental primers with varying monomer concentrations. All mixtures were thoroughly homogenized before use by manual stirring with a sterile spatula (or mechanical mixing at a controlled speed, where applicable) for a standardized duration until a visually uniform consistency without streaks or unmixed regions was achieved.

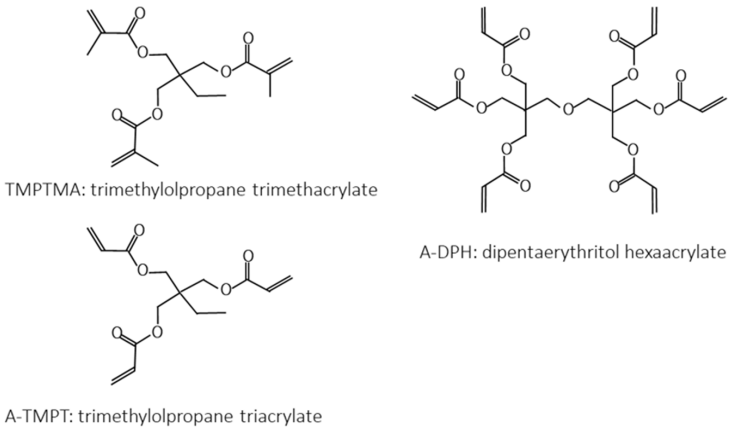


Figure 1. Structural formulas of acrylate monomers used in this study.

2.3. SBS Test

A total of 114 specimens of PEEK (Shofu Inc., Kyoto, Japan) were used (n = 6 per group). The specimens were divided into experimental primer groups consisting of three types of primers, each at five different concentrations (100, 200, 300, 400, and 500 μL), as well as a control group without primer application. Additionally, for the 500 μL addition groups of each primer, an extra set of specimens was stored in distilled water at 37 ± 2 °C for 3 months to evaluate the effect of long-term water storage; this condition was selected for stability assessment because it demonstrated the most favorable initial performance. To characterize the bonding surface of PEEK prior to primer application, transmission electron microscopy (TEM (200 kV TEM, JEM-2100, JEOL, Tokyo, Japan)) was performed for microstructural observation, scanning transmission electron microscopy (STEM (200 kV STEM, JEM-2100F, JEOL)) coupled with elemental analysis was conducted to evaluate the elemental composition, and X-ray diffraction (XRD (CuKα XRD; RINT2500, Rigaku, Tokyo, Japan)) analysis was carried out to assess crystallinity.

Each specimen's adhesive surface was polished under water irrigation using #2000 silicon carbide abrasive paper (Struers A/S, Rodovre, Denmark). The mirror polished surfaces were treated with the experimental prepared primer for 20 s, and then the surface was gently air-dried with oil-free compressed air for another 20 s. After light-curing for 10 s,

a stainless steel rod (3.6 mm diameter, 2.0 mm height) was luted onto the pretreated surface using an auto-mixed, dual-cure luting resin cement (PANAVIA V5, Kuraray Noritake Dental, Tokyo, Japan). Cementation was carried out using a detachable Teflon jig mold, where a 10 N load was applied and maintained for 3 min (Figure 2). The 10 N load was standardized using a manual loading device while being continuously verified. Bonded specimens were light-cured for 20 s on each side from two opposite sides.

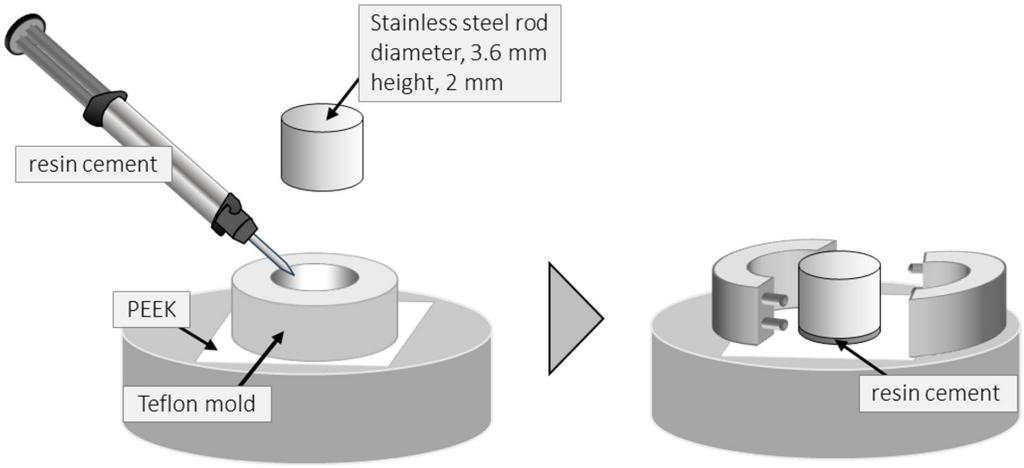


Figure 2. Schematic illustration of fabrication of test samples. Luting resin cement was built up on an adhesive surface with a detachable Teflon jig mold after pretreatment with an experimental solution.

The SBS value was measured using a universal testing machine (Autograph AG-X, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/min (Figure 3). Stress at failure was calculated automatically using the system software. Post-fracture analysis was conducted using a light microscope (SMZ-10; Nikon, Tokyo, Japan) to classify the failure mode into one of the following categories: adhesive failure at the resin–PEEK interface (AF), cohesive failure within the resin cement (CF), and mixed adhesive–cohesive failure (MF). Statistical analysis was performed using the Kruskal–Wallis test and Steel–Dwasss multiple comparison test, as the data lacked homogeneity of variance ($p < 0.05$) according to Levene's test. The significance level was set at 5%.

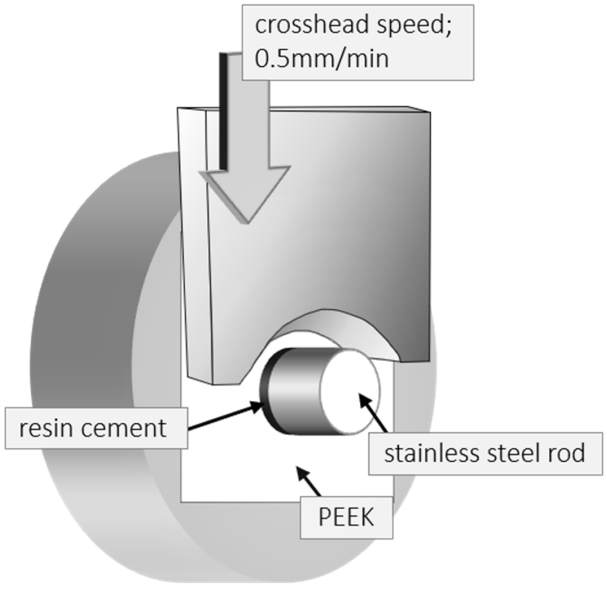


Figure 3. Shear bond strength was measured using a universal testing machine with a crosshead speed of 0.5 mm/min.

3. Results

The surface morphology and composition of untreated PEEK were first characterized prior to primer application. TEM observations revealed that the PEEK surface was predominantly homogeneous, with scattered dark spots corresponding to pigment particles (Figure 4). STEM coupled with elemental analysis confirmed that most of these particles consisted of titanium dioxide with a rutile crystal structure. Aluminum was detected on the TiO_2 particles, while chromium and antimony were only rarely observed in the area (Figure 5). XRD analysis showed the characteristic diffraction peaks of PEEK, along with additional peaks corresponding to rutile-phase titanium dioxide, indicating the presence of TiO_2 within the material (Figure 6).

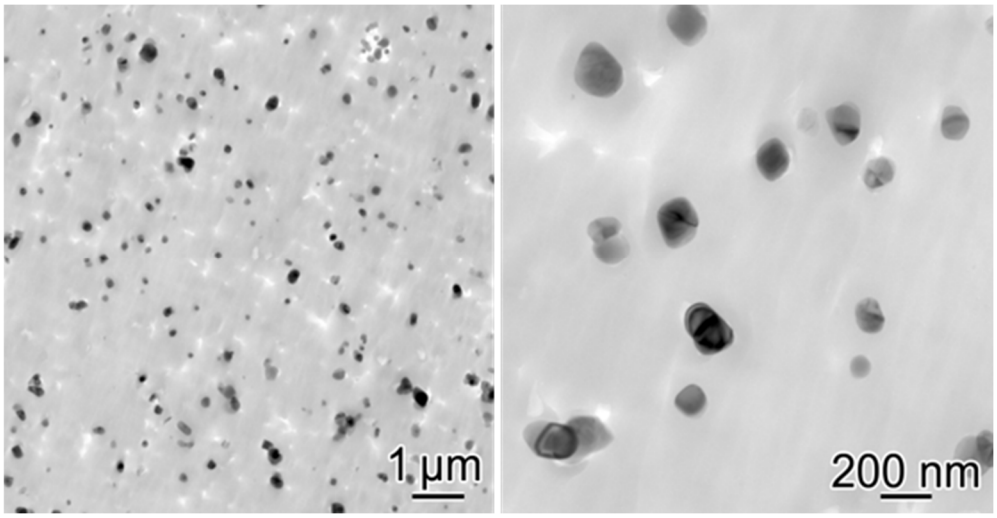


Figure 4. TEM images of PEEK. Dark particles are embedded in the PEEK matrix.

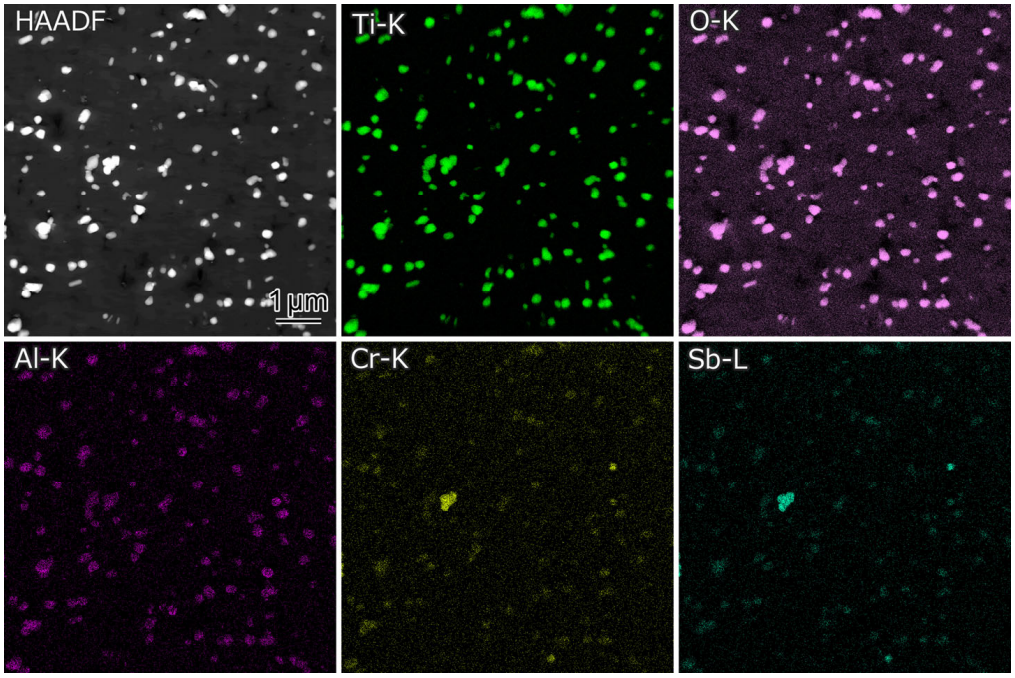


Figure 5. STEM-HAADF image and corresponding elemental maps of the PEEK. HAADF image illustrating bright particles embedded within the PEEK matrix. Elemental maps of Ti-K, O-K, Al-K, Cr-K, and Sb-L confirm that these bright particles consist of the respective elements.

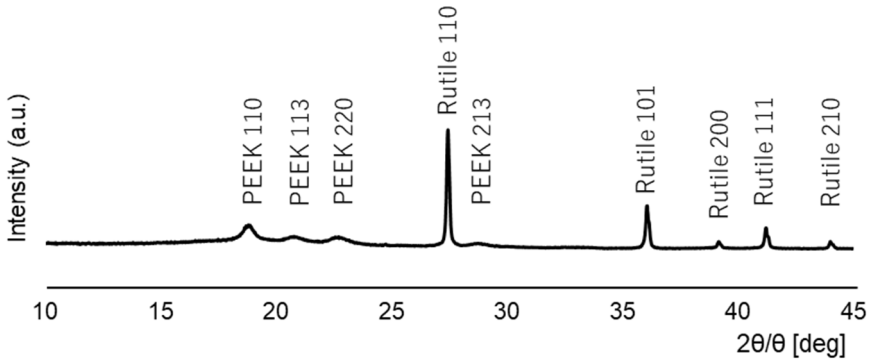


Figure 6. XRD pattern of the PEEK composite. Distinct diffraction peaks of PEEK and rutile (TiO_2) are observed, confirming the presence of both the polymer matrix and the rutile phase within the composite.

The SBS (median [Q1–Q3] MPa) results for all experimental groups are summarized in Figure 7. The control group exhibited a median bond strength of 9.5 [8.5–12.8] MPa. Incorporation of TMPTMA at concentrations ranging from 100 to 500 μL yielded median SBS values between 10.3 [7.8–11.5] and 12.2 [10.4–13.8] MPa. Although minor increases were observed at intermediate concentrations, no statistically significant differences were detected among the TMPTMA groups or in comparison with the control ($p > 0.05$).

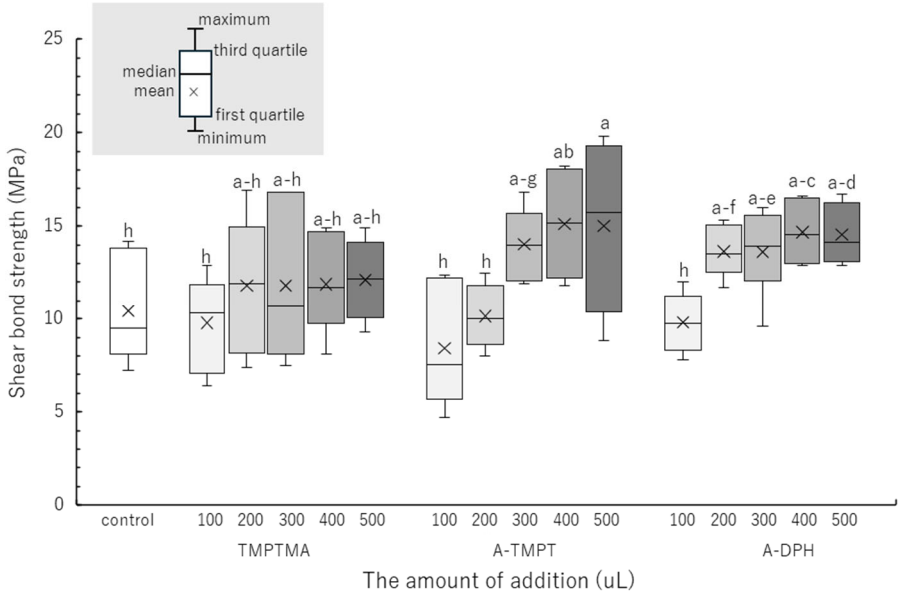


Figure 7. Shear bond strength values (MPa) of each group (upper) and failure mode (bottom) of FC. In the boxplot graph (upper), the horizontal line represents the median (50%), symbol "×" represents the mean. Same letters (a–h) in each column are not significantly different ($p > 0.05$) in shear bond strength values based on the Kruskal–Wallis test ($p < 0.05$) and Steel–Dwass multiple comparison test ($p < 0.05$).

For the A-TMPT groups, SBS values ranged from 7.6 [6.4–11.1] to 15.8 [11.7–18.7] MPa. Groups treated with 300–500 μL of A-TMPT exhibited significantly higher SBS values than the control and the 100 and 200 μL groups ($p < 0.05$). Similarly, the A-DPH groups demonstrated median SBS values ranging from 9.8 [8.6–10.9] to 14.6 [13.4–16.0] MPa across all concentrations, with statistically significant increases relative to the control and the 100 μL A-DPH group ($p < 0.05$).

The distribution of failure modes following shear testing is shown in Figure 8. The control group predominantly exhibited MF. Across all concentrations of TMPTMA, A-

TMPT, and A-DPH, mixed failure remained the major failure pattern, with only occasional occurrences of AF.

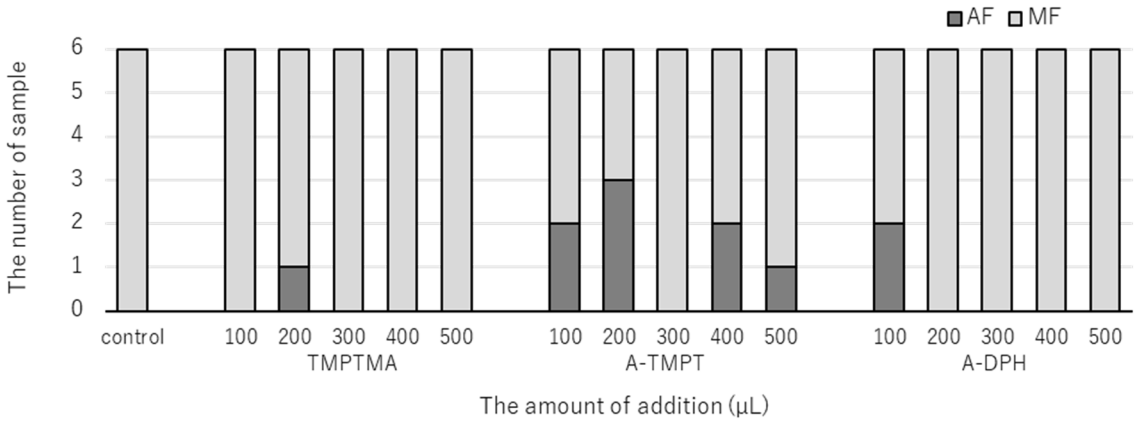


Figure 8. Distribution of failure modes after test. AF and MF indicate adhesive failure and mixed failure, respectively.

After three months of underwater storage (Figure 9), the SBS values of the groups with 500 μL additions of A-TMPT and A-DPH were 8.6 [6.8–10.3] to 6.2 [5.1–9.6] MPa, respectively, with no significant difference observed between the groups ($p > 0.05$). Fractographic analysis revealed predominantly interfacial failures in all specimens, except for one mixed failure observed in group A-DPH.

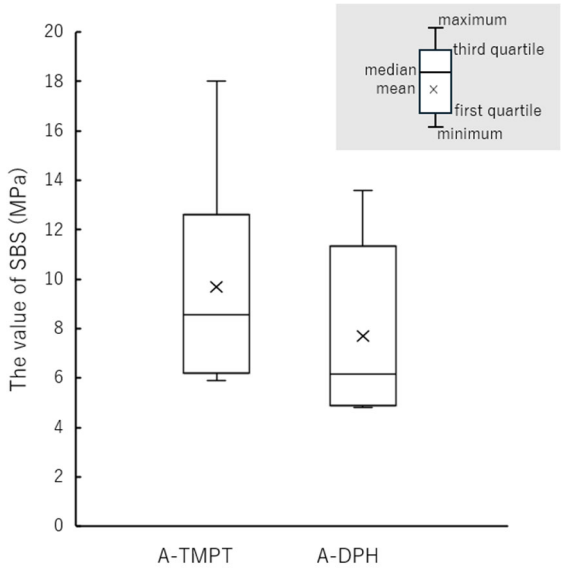


Figure 9. Shear bond strength values (MPa) of the groups with 500 μL additions of A-TMPT and A-DPH after three months of water storage without significantly different ($p > 0.05$) based on the Kruskal–Wallis test ($p < 0.05$) and Steel–Dwass multiple comparison test ($p < 0.05$). In the boxplot graph (upper), the horizontal line represents the median (50%), symbol "×" represents the mean.

4. Discussion

The present study aimed to investigate the effectiveness of multifunctional methacrylate and acrylate monomers in a base primer for enhancing the 24 h shear bond strength (SBS) of resin cement to PEEK surfaces. PEEK is a high-performance polymer with high crystallinity, low surface energy, and chemical inertness, which make durable adhesive bonding inherently challenging. These intrinsic surface properties are critical determinants of interfacial adhesion because they limit the availability of reactive functional groups and reduce surface wettability, thereby directly constraining resin–substrate interaction.

Understanding strategies to improve its adhesion is crucial for expanding its applications in restorative dentistry and medical devices. In this study, a commercially available PEEK material was characterized using TEM, which revealed that the untreated PEEK surface was predominantly homogeneous, with scattered dark spots corresponding to pigment particles. STEM coupled with elemental analysis confirmed that most of these particles consisted of titanium dioxide with a rutile crystal structure, while trace amounts of aluminum, chromium, and antimony were detected. XRD analysis further showed characteristic diffraction peaks of PEEK, along with additional peaks attributable to rutile-phase titanium dioxide. Although these TiO_2 particles introduce minor surface heterogeneity, their contribution is primarily physical rather than chemical, as they do not provide functional groups capable of participating in covalent bonding with methacrylate- or acrylate-based monomers. Consequently, even primers incorporating multifunctional monomers exhibited limited improvements in early shear bond strength. As expected, the generally low bond strengths observed across all groups reflect the inherently low surface energy, chemical inertness, and highly crystalline structure of PEEK. These characteristics reduce the density of available functional groups for chemical interaction with resin-based adhesives and thus pose a substantial challenge to achieving durable bonding. From a mechanistic standpoint, the adhesion behavior in this system is primarily governed by the absence of chemical reactivity at the PEEK surface; therefore, interfacial bonding is expected to rely predominantly on physical interactions and limited mechanical interlocking rather than covalent bonding. Although slight improvements were detected with the acrylate-containing primers, the incorporation of multifunctional monomers could produce a statistically significant enhancement in early SBS. This suggests that the chemical reactivity provided by these monomer species alone is insufficient to overcome the intrinsic adhesion-resistant nature of PEEK. From a mechanistic perspective, the adhesion behavior observed in this study may be attributed to limited interfacial chemical interactions, where multifunctional methacrylate and acrylate monomers primarily contribute through polymer network formation within the adhesive layer rather than direct covalent bonding to the chemically inert PEEK surface.

The addition of TMPTMA, a multifunctional methacrylate monomer, to the base primer resulted in SBS values ranging from approximately 10 to 12 MPa across the tested concentrations, with modest but statistically non-significant increases at intermediate volumes (200–400 μL). TMPTMA is theoretically capable of generating highly cross-linked polymer networks within the resin cement, potentially enhancing internal cohesion and contributing to improved early mechanical properties [25]. Importantly, this effect is primarily related to bulk resin strengthening rather than interfacial adhesion enhancement. Nonetheless, polished PEEK surfaces inherently lack reactive functional groups such as hydroxyl or carboxyl moieties, severely limiting the formation of covalent bonds with methacrylate functional groups. This limitation is well-documented in the literature: high-performance polymers such as PEEK exhibit low surface energy and pronounced chemical inertness, resulting in poor direct adhesion with methacrylate-based systems unless more aggressive surface treatments are employed. Primers combining MMA with other functional monomers, such as UDMA, have been shown to improve SBS values and mitigate reductions after thermocycling, underscoring the potential benefits of incorporating multiple reactive monomer species [19]. Additionally, pre-treatments such as photo-induced grafting of methacrylate monomers have been demonstrated to enhance adhesion by introducing reactive polymer brushes on the PEEK surface, producing significant increases in bond strength relative to untreated controls [26]. In the present study, although TMPTMA may reinforce the cohesive integrity of the resin cement itself, its contribution to interfacial chemical bonding is minimal, accounting for the absence of significant improvements in

early SBS. The modest increases observed at intermediate monomer volumes may reflect an optimal balance between surface wetting and cross-link density, whereas excessive volumes may elevate viscosity and impede penetration into micro-topographical surface features, consistent with prior observations in methacrylate primer optimization for low-energy polymers. These findings are in line with previous studies reporting that commercial PEEK primers containing phosphate or methacrylate functional monomers (e.g., 10-MDP-based systems) can improve initial bond strength, particularly when combined with airborne-particle abrasion or sulfuric acid etching, although durable long-term adhesion remains challenging without surface activation.

Acrylate-doped primers, specifically A-TMPT and A-DPH, elicited statistically significant increases in SBS at higher monomer volumes (300–500 μL), attaining values approaching 16 MPa, whereas lower concentrations remained comparable to the control (7.6–11.1 MPa for A-TMPT; 9.8–10.9 MPa for A-DPH; $p > 0.05$). Acrylate monomers are widely used in industrial coatings and photosensitive resin systems due to their high radical polymerization reactivity [27–29]. The acrylate functional group consists of a vinyl C=C bond conjugated with a carbonyl (C=O) group, where the polar carbonyl moiety enhances electron distribution and facilitates radical formation, resulting in rapid polymerization kinetics. Accordingly, the primary contribution of acrylate monomers in this study is attributed to their rapid polymerization behavior and improved wetting ability rather than chemical interaction with PEEK. Based on these intrinsic chemical characteristics, acrylate-based primers were investigated in this study to evaluate whether their high reactivity and low viscosity could improve surface wetting and early interfacial polymer network formation even on chemically inert, untreated PEEK substrates. This approach was intended to assess whether monomer-driven interfacial effects could partially compensate for the absence of surface activation treatments such as plasma or chemical etching. Acrylate monomers generally possess lower viscosity and faster polymerization kinetics relative to methacrylates, facilitating enhanced surface wetting and more efficient initial network formation upon polymerization [30]. These favorable rheological and kinetic characteristics likely account for the observed improvements in early bond strength at higher concentrations. Nevertheless, the magnitude of the enhancement, although statistically significant, remains moderate, indicating that the intrinsic low surface energy and chemical inertness of polished PEEK continue to impose substantial constraints on adhesive performance. Furthermore, acrylate-based systems are more susceptible to hydrolytic degradation compared with methacrylate analogs, a factor reported to compromise long-term interfacial durability in other polymeric adhesive systems [22]. Within the context of PEEK adhesion, this susceptibility suggests that, although acrylates may improve initial wetting and early stress distribution at the interface, their impact on long-term bond stability is uncertain. Consequently, surface modification strategies aimed at simultaneously enhancing chemical functionality and micromechanical interlocking—such as sandblasting, plasma activation, or chemical etching—remain critical for achieving durable adhesion. In the present study, while higher concentrations of acrylate primers promoted improved interfacial coverage and statistically significant increases in early SBS, the absence of consistent trends across all monomer concentrations further emphasizes that monomer chemistry alone cannot fully compensate for the scarcity of reactive surface groups on PEEK. From a mechanistic standpoint, the improved performance of acrylate-containing primers at higher concentrations may be associated with enhanced radical propagation efficiency and increased interfacial polymerization rate, which can temporarily improve interfacial sealing and stress transfer at the early stage of bonding.

Mechanistically, the limited effects of both methacrylate and acrylate comonomers can be attributed to the interplay of surface chemistry, monomer reactivity, and polymeriza-

tion kinetics. Polished PEEK surfaces lack functional groups capable of forming covalent bonds with either methacrylate or acrylate moieties, severely restricting interfacial polymer network formation. Although multifunctional monomers may enhance cross-link density within the resin cement layer itself, this reinforcement does not necessarily translate to improved interfacial adhesion. This interpretation is supported by failure-mode analysis, which revealed predominantly mixed adhesive–cohesive failures across all primer types and concentrations, suggesting that adhesive strength was governed primarily by the mechanical properties of the resin cement rather than chemical bonding to PEEK. Similar failure patterns have been reported in studies using commercial PEEK primers and mechanically treated surfaces, where mixed failures predominate despite surface roughening or chemical conditioning, further supporting the limited chemical reactivity of untreated PEEK. These failure patterns further support the conclusion that interfacial adhesion, rather than cohesive resin strength, is the primary limiting factor in the present system.

It should be emphasized that the present study assessed only 24 h SBS to evaluate early retention, and the long-term durability of these bonds under hydrolytic, thermal, and mechanical stresses was not systematically investigated. Therefore, the present findings should be interpreted within the limitations of short-term in vitro evaluation and should not be directly extrapolated to predict long-term clinical performance. Furthermore, polished PEEK surfaces were employed, whereas clinical practice often incorporates surface roughening prior to cementation. Therefore, future studies examining the potential synergistic effects of surface roughening combined with multifunctional monomer primers are warranted. Such combined strategies are expected to enhance both micromechanical interlocking and chemical interaction, potentially overcoming the inherent adhesion limitations of PEEK. Finally, variations in base primer composition—including solvent type, photoinitiator concentration, and monomer ratios—may influence monomer penetration and polymerization efficiency, suggesting that further optimization of primer formulations could enhance adhesive performance and long-term bond stability. In addition, the potential biological effects and cytotoxicity of multifunctional methacrylate and acrylate monomers should be carefully considered for dental applications. Incomplete polymerization may result in the release of residual unreacted monomers over time, which could contribute to local cytotoxic, inflammatory, or degradative effects within the oral environment. Therefore, further investigations evaluating the degree of conversion, monomer elution, and long-term biocompatibility of these experimental primer formulations are warranted before clinical application. Taken together, these findings provide mechanistic insight into the limited early bonding improvements conferred by multifunctional monomers and highlight the critical role of PEEK's intrinsic surface properties in governing adhesive performance. The results underscore that, while primer chemistry can modulate initial bond strength, achieving clinically relevant and durable adhesion to PEEK will likely require a combination of tailored surface treatments and optimized adhesive formulations, offering a clear direction for future research and potential clinical application. To address the limitations of the present study, future studies should focus on evaluating the synergistic effects of multifunctional methacrylate or acrylate primers combined with surface treatments such as airborne-particle abrasion, plasma activation, or chemical etching to improve adhesion to PEEK. Long-term durability under thermocycling, water storage, and mechanical fatigue should also be investigated to better simulate clinical conditions. In addition, optimization of primer formulation and assessment of biocompatibility and monomer elution are necessary to ensure both adhesive performance and clinical safety. Furthermore, the absence of in vivo validation and artificial aging protocols represents an important limitation of the present in vitro study, and future research incorporating these aspects is essential to better establish the clinical relevance and durability of the observed bonding behavior.

5. Conclusions

Although the addition of multifunctional methacrylate or acrylate monomers did not significantly improve 24 h SBS to PEEK surfaces, acrylate-containing primers at higher concentrations were able to confer modest enhancements. The study highlights the limited effectiveness of multifunctional monomers in isolation and underscores the necessity of comprehensive adhesive strategies that combine mechanical surface modification with chemical activation to achieve improved laboratory bonding performance to PEEK. However, given the in vitro nature of this study, direct clinical extrapolation should be made with caution. These findings may have potential implications for primer design in dental applications, but further studies including artificial aging and in vivo validation are required to confirm clinical relevance.

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