

Article

Concentration-Dependent Synergistic Interfacial Interactions Between Multifunctional Acrylate and Silane Coupling Agents in an Organic–Inorganic Nanohybrid Material

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Abstract

Synergistic effects of a multifunctional acrylate and a long-chain silane coupling agent were investigated in an organic–inorganic nanohybrid material. We tested the bond strength of nanohybrid composites treated with experimental primers containing silane coupling agents—3-methacryloxypropyl trimethoxysilane (γ -MPTS) or 8-methacryloxyoctyl trimethoxysilane (8-MOTS)—with or without multifunctional acrylates—trimethylolpropane triacrylate (A-TMPT) or dipentaerythritol hexaacrylate (A-DPH). Shear bond strength was evaluated after 24 h of water storage at 37 °C. Untreated control and silane-only groups exhibited low shear bond strengths (e.g., control: 2.4 ± 2.0 MPa) and failed exclusively at the adhesive interface. While addition of A-TMPT did not significantly improve bond strength, addition of A-DPH produced significantly higher shear bond strengths. Highest strength was achieved with 30% 8-MOTS and A-DPH (22.4 ± 6.1 MPa), followed by 20% γ -MPTS and A-DPH (19.0 ± 7.0 MPa), and A-DPH groups produced cohesive failures. Regardless of the silane used (γ -MPTS or 8-MOTS), incorporating A-DPH in the primer consistently yielded superior bond strengths, indicating a promising strategy for improved adhesion for such nanohybrid systems. These findings provide new insights into optimizing resin–filler interfacial interactions and may contribute to the development of restorative materials with improved long-term clinical durability.

Keywords: silane coupling; multifunctional acrylate; bond strength; resin



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1. Introduction

The development of organic–inorganic nanohybrid dental materials has attracted considerable attention due to their ability to integrate the advantageous properties of polymeric matrices with inorganic nanoparticles. Such composites provide enhanced mechanical strength, superior esthetics, and long-term durability, which are critical for the demanding

oral environment. Nanohybrid composites have been increasingly engineered to tailor functional properties such as polymerization shrinkage, translucency, and wear resistance by optimizing filler size distribution, surface chemistry, and filler-matrix interactions [1]. A key determinant of performance is the resin matrix–nanofiller interface, which is largely governed by surface pretreatments that facilitate strong chemical and mechanical bonding between organic polymers and inorganic fillers, including silica, alumina, and zirconia nanoparticles. Efficient interfacial bonding strengthens mechanical properties, mitigates water uptake, reduces microcrack initiation, and enhances long-term stability in the oral environment [2].

Chemical coupling between resin matrices and inorganic fillers is typically mediated by silane coupling agents that act as molecular bridges, covalently bonding to hydroxyl groups on filler surfaces while simultaneously copolymerizing with resin monomers. 3-methacryloxypropyl trimethoxysilane (γ -MPTS) remains the gold standard due to its bifunctional nature: hydrolyzable methoxy groups allow strong attachment to filler surfaces, while the methacrylate moiety copolymerizes with acrylate resins, ensuring a durable and stable interface [3–5]. Extensive studies have confirmed that silane treatment not only improves bond strength but also reduces filler agglomeration and clustering, thereby enhancing the mechanical behavior, surface integrity, and wear resistance of dental composites [6]. The effectiveness of silane treatment depends on proper hydrolysis, concentration, and uniform application, highlighting the need for optimized surface pretreatment protocols.

More recently, 8-methacryloxyoctyl trimethoxysilane (8-MOTS), with an extended eight-carbon alkyl spacer compared to the three-carbon spacer in γ -MPTS, has shown promise in enhancing interfacial properties. The longer alkyl chain increases flexibility and hydrophobicity, improving mechanical compliance and resistance to hydrolytic degradation by reducing water penetration at the resin-filler boundary. 8-MOTS may also promote more uniform silane coverage, improved filler dispersion, and better handling characteristics during composite formulation [7,8]. Furthermore, the specific structure of the silane spacer influences composite consistency and polymerization behavior, suggesting that tailored silane architectures can optimize both processing and performance [1]. Silane concentration critically affects interfacial bonding: suboptimal amounts result in incomplete coverage and weak bonding, while excessive silane forms multilayers that reduce interfacial strength, increase water sorption, and can act as plasticizers within the composite matrix [4,9–14]. Optimal silane concentration ranges maximize fracture toughness, minimize water sorption, and ensure consistent mechanical performance, particularly with high-surface-area nanofillers and highly functionalized resin systems.

Multifunctional acrylate and methacrylate monomers, containing two or more polymerizable vinyl groups, are fundamental in formulating advanced dental composites capable of forming densely crosslinked polymer networks via free-radical polymerization. This crosslinking enhances mechanical strength, dimensional stability, wear resistance, and long-term durability. Methacrylate monomers, such as Bis-GMA and UDMA, allow controlled polymerization, reduced shrinkage stress, and formation of stiff, thermally stable networks. In contrast, multifunctional acrylates such as trimethylolpropane triacrylate (A-TMPT) and dipentaerythritol hexaacrylate (A-DPH) exhibit higher reactivity and enable dense network formation, improving flexural strength, modulus, wear resistance, and hydrolytic stability in the oral environment [15–21]. The combination of different monomers can fine-tune mechanical properties, polymerization kinetics, and handling characteristics, offering versatility for clinical applications.

The synergistic integration of silane coupling agents with multifunctional monomers is critical for optimizing the mechanical performance and interfacial durability of organic–inorganic nanohybrid composites [22]. The chemical environment during

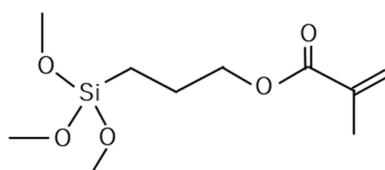
formulation—including monomer acidity, filler surface chemistry, and photoinitiator systems—can significantly affect silane hydrolysis, condensation, and network formation, thereby influencing the resulting interface and mechanical performance [2]. Careful control of formulation conditions, including the use of longer-alkyl-chain silanes and highly functional monomers, can fine-tune the resin-filler interface, balancing rigidity with flexibility to resist microcracking and fatigue failure. Recent systematic reviews also demonstrate that silane application improves repair bond strength in methacrylate-based composites, reinforcing the clinical relevance of interface optimization [2,14,23].

In this study, we investigated whether an optimal concentration range existed for silane coupling agents, which could maximize resin-filler interfacial bonding and mechanical durability in nanohybrid composites formulated with highly functional acrylate monomers. Although previous studies have examined silane types and concentrations, studies combining silane treatment with highly functional acrylate monomers are scarce and appear to be largely unreported. We hypothesized that concentrations below or above this threshold range could compromise interfacial performance and hydrolytic resistance due to inadequate surface coverage or excessive silanization, respectively. This study therefore aims to explore this relatively unexamined area, providing insight into the interaction between silane and acrylate monomers for optimizing nanohybrid composite formulation. By identifying optimal silane concentrations, our findings may help improve the longevity and mechanical performance of resin-based dental composites.

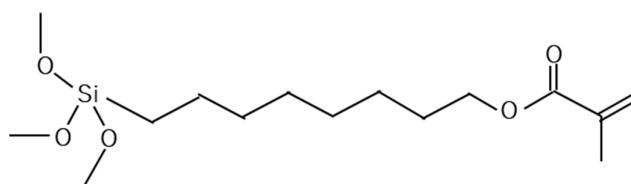
2. Materials and Methods

2.1. Experimental Primer Preparation

The experimental primer was prepared using two separate components: a silane coupling agent solution and a monomer liquid. The silane solution consisted of either 3-methacryloxypropyl trimethoxysilane (γ -MPTS, Shin-Etsu Chemical, Tokyo, Japan; Figure 1) or 8-methacryloxyoctyl trimethoxysilane (8-MOTS, Shin-Etsu Chemical, Tokyo, Japan; Figure 1), dissolved in ethanol at final concentrations of 10%, 20%, 30%, or 40% (v/v). Immediately before application, each silane solution was activated via hydrolysis using a 2 wt% acetic acid in ethanol solution (Wako Pure Chemical Industries, Osaka, Japan) in equal volumes.



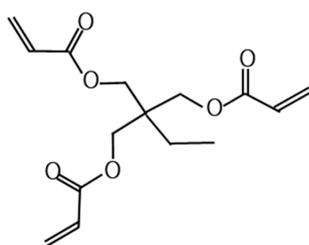
γ -methacryloxypropyl trimethoxy silane (γ -MPTS)



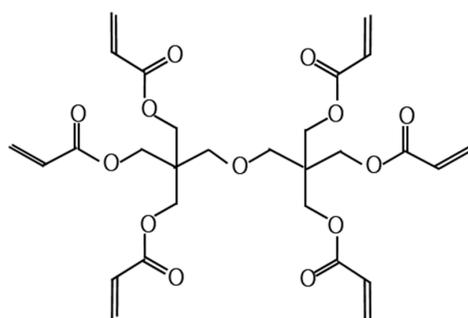
8-methacryloxyoctyl trimethoxy silane (8-MOTS)

Figure 1. Structural formulas of silane coupling agents of γ -MPTS and 8-MOTS used in this study.

The monomer liquid was composed of 60 wt% multifunctional acrylate, using either trimethylolpropane triacrylate (A-TMPT, Shin-Nakamura Chemical, Wakayama, Japan; Figure 2) or dipentaerythritol hexaacrylate (A-DPH, Shin-Nakamura Chemical, Wakayama, Japan; Figure 2), combined with 23 wt% methyl methacrylate (MMA, Mitsubishi Chemical, Tokyo, Japan), 15 wt% acetone (Wako Pure Chemical, Industries, Osaka, Japan), and 2 wt% camphorquinone (Tokyo Chemical Industry, Tokyo, Japan) as the polymerization initiator. All components were mixed in an amber bottle using a vortex mixer for 5 min until homogeneous.



A-TMPT: trimethylolpropane triacrylate (A-TMPT)



A-DPH: dipentaerythritol hexaacrylate (A-DPH)

Figure 2. Structural formulas of acrylate monomers of A-TMPT and A-DPH used in this study.

2.2. Shear Bond Strength Testing

A total of 125 specimens of an organic–inorganic nanohybrid composite material were used. A control group was included, in which specimens received no primer treatment. The remaining specimens were subjected to silane and monomer treatment.

According to information provided by the manufacturer (KATANA AVENCIA Block, Kuraray Noritake Dental, Tokyo, Japan), the material contained inorganic nanoparticle fillers, which were mainly composed of 20 nm alumina filler and 40 nm silica filler. Specimens were sectioned using a low-speed diamond saw under water cooling, ensuring that the thickness of each block was at least 5 mm. Each specimen was embedded in a resin ring (Ring forms, Buehler, Lake Bluff, IL, USA) with was carefully embedded in Epofix resin (Struers A/S, Rodovre, Denmark), ensuring the bonding surface was positioned as parallel as possible to the mold base. Each specimen’s adhesive surface was polished under water irrigation using silicon carbide abrasive papers of gradually increasing fineness, finishing with #2000 (Struers A/S, Rodovre, Denmark) using a rotary polishing machine at 300 rpm to standardize surface roughness, followed by ultrasonic cleaning in distilled water for 5 min, and air-dried with oil-free compressed air for 10 s.

The polished surface was treated with the activated silane solution using a disposable microbrush to ensure uniform coverage and left undisturbed for 30 s. Excess solvent was removed using mild-pressure and oil-free compressed air from a distance of 10 cm for

10 s. Subsequently, the monomer liquid was applied with a disposable microbrush to the silanized surface for 30 s. The surface was then air-dried using high-pressure and oil-free compressed air for 10 s to evaporate residual solvents. Polymerization was then carried out with a light-curing unit (Pencure 2000, Morita, Tokyo, Japan) at an intensity of 1200 mW/cm² for 20 s.

Luting resin cement (PANAVIA Veneer LC, Kuraray Noritake Dental, Tokyo, Japan) column was built up onto the treated surface using a detachable Teflon jig mold to form a resin cement cylinder measuring 2 mm in thickness and 3.6 mm in diameter (Figure 3). Polymerization was performed using a light-curing unit (Pencure 2000) for 20 s. All specimens were stored in distilled water at 37 ± 2 °C for 24 h prior to mechanical testing. Shear bond strength (SBS) was measured using a universal testing machine (Autograph AG-X, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/min (Figure 4). Stress at failure was calculated automatically using the system software. Post-fracture analysis was conducted using a light microscope (SMZ-10, Nikon, Tokyo, Japan) at ×4 magnification to examine the fractured interface, and the failure mode was classified into one of the following categories: a; Adhesive failure at the resin–substrate interface, b; mixed failure involving adhesive failure at the resin–substrate interface and cohesive failure within the resin cement, and c; cohesive failure within the substrate material (Figure 5). Statistical analysis was performed using IBM SPSS Statistics 29 (IBM Corp., Armonk, NY, USA). Two-way analysis of variance was used to evaluate the effects of silane and monomer application, as well as their interaction, on the shear bond strength. Multiple pairwise comparisons were performed using Tukey’s post hoc test, with significance set at $p < 0.05$.

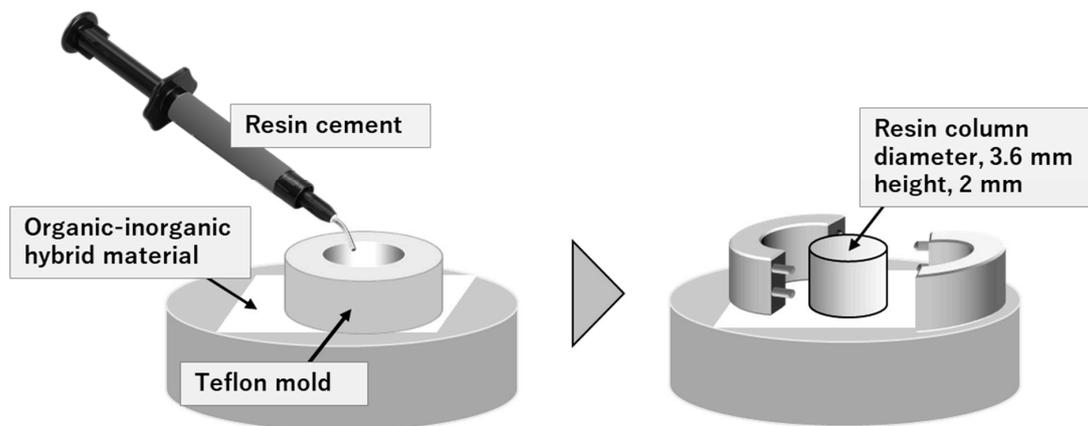


Figure 3. Schematic illustration of the fabrication of test samples. Luting resin cement was built up on an adhesive surface with a detachable Teflon jig mold after pretreatment with an experimental solution.

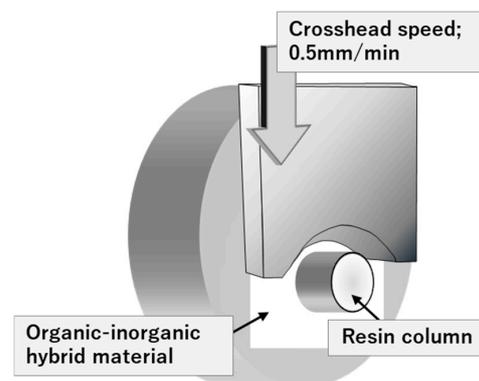


Figure 4. Shear bond strength between the substrate material and resin column was measured using a universal testing machine with a crosshead speed of 0.5 mm/min.

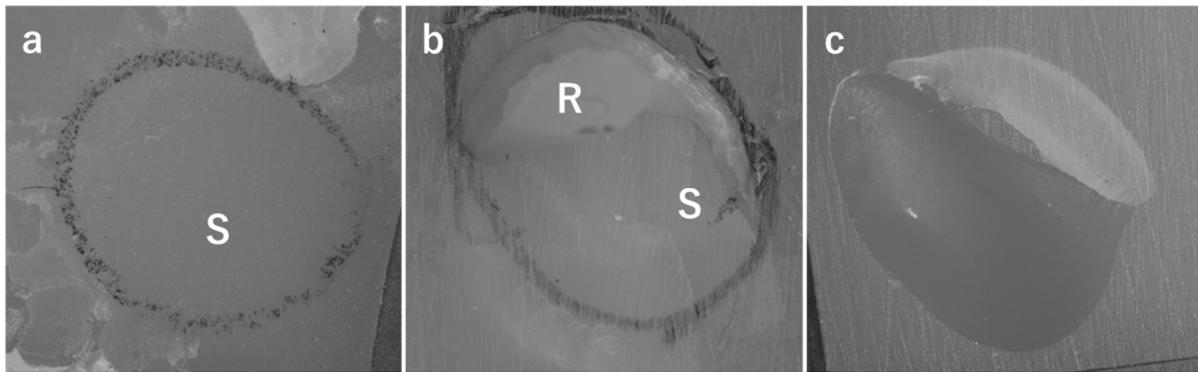


Figure 5. (a) Adhesive failure, showing complete debonding between the substrate material and the resin column. (b) mixed failure involving adhesive failure at the substrate material interface and cohesive failure within the resin column. (c) cohesive failure within the substrate material itself. S indicates the substrate material, and R indicates the residual resin column.

3. Results

Figure 6 presents the SEM images of the material surface intended for bonding, revealing the presence of nano-sized structures enriched with fillers. The shear bond strength values (mean \pm SD MPa) and corresponding failure modes of all groups are presented in Figures 7 and 8, and Table 1. The untreated control group exhibited the lowest shear bond strength (2.4 ± 2.0 MPa), with all its specimens demonstrating adhesive failure at the bond interface.

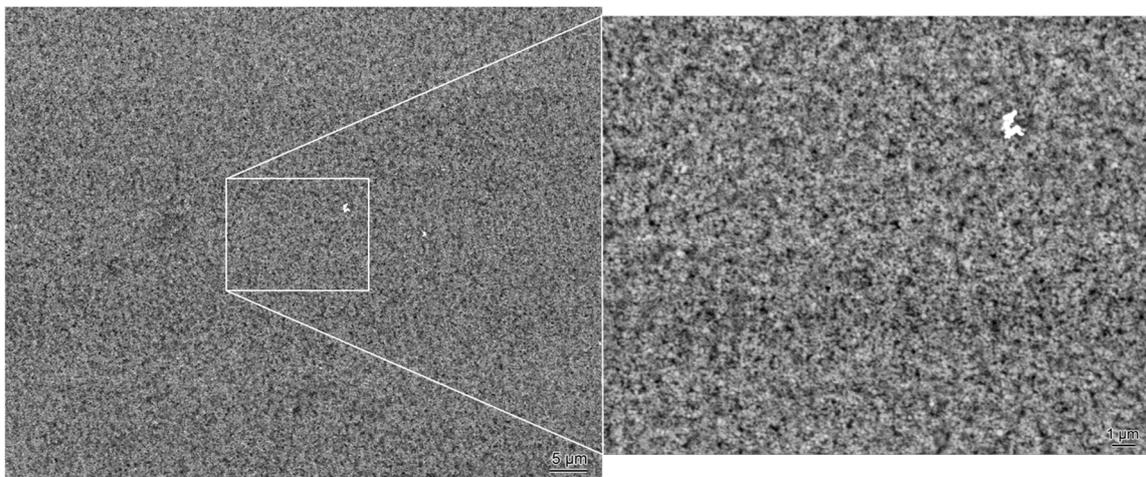


Figure 6. SEM images of organic–inorganic nanohybrid composite material consisted by nanoparticle fillers.

Application of silane coupling agents without acrylate monomer did not result in significantly improved bond strength compared to the control ($p > 0.05$). The highest shear bond strength value observed among the silane-only groups was 6.6 ± 0.8 MPa for 30% γ -MPTS and 3.6 ± 1.3 MPa for 20% 8-MOTS. Similar to the control group, all silane-only specimens exhibited adhesive failures.

The incorporation of A-TMPT into the silane treatment resulted in shear bond strength values that were comparable to or slightly higher than those of the corresponding silane-only groups. However, the differences were not statistically significant within each silane group ($p > 0.05$). In contrast, the addition of A-DPH consistently yielded significantly higher bond strengths than both the silane-alone and silane + A-TMPT groups ($p < 0.05$). The highest shear bond strength value was achieved with the combination of 30% 8-MOTS

and A-DPH (22.4 ± 6.1 MPa), followed by 20% γ -MPTS and A-DPH (19.0 ± 7.0 MPa). Notably, cohesive failure, rather than adhesive failure, was observed in some specimens treated with A-DPH.

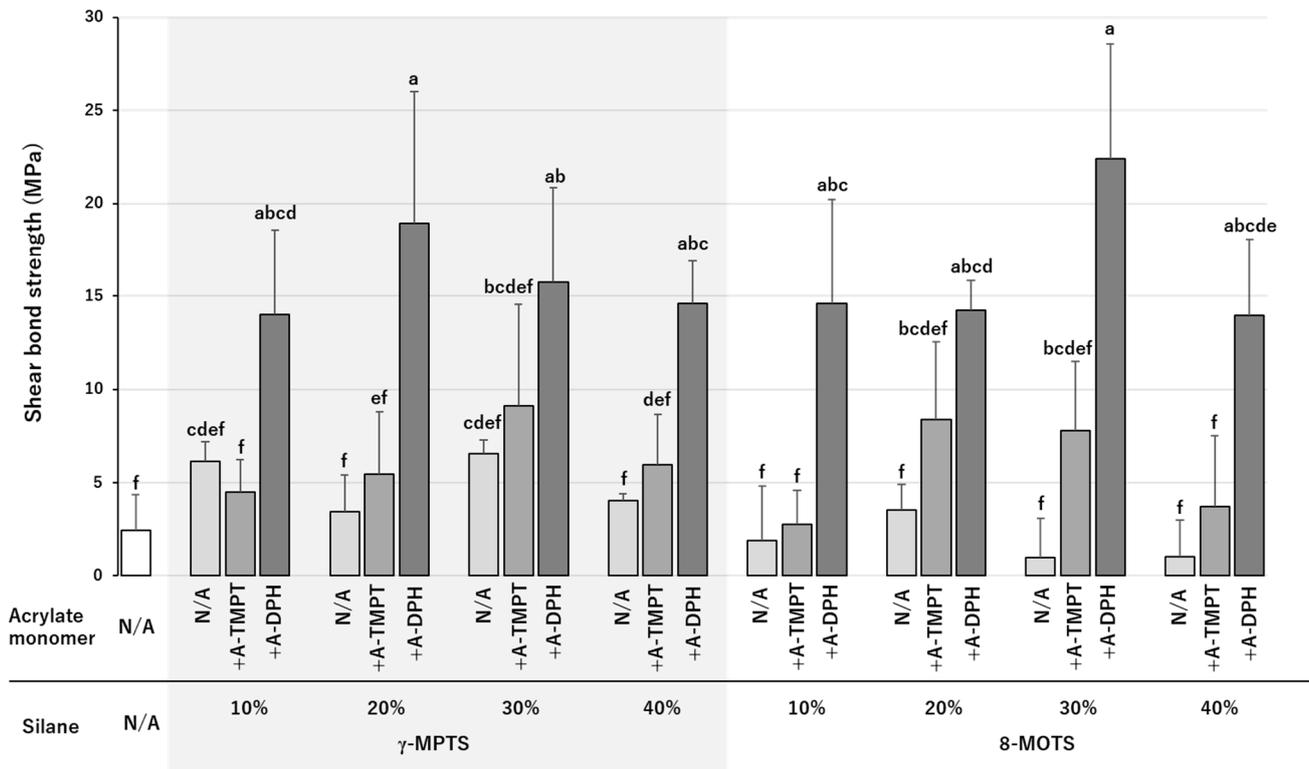


Figure 7. Shear bond strength values (mean and standard deviation, MPa) of each group. The gray area on the left side shows the results for γ -MPTS, and the right-sided white area shows the results for 8-MOTS. The horizontal axis shows the conditions for the silane coupling agent and acrylate monomer. The same letters (a–f) in each column are not significantly different ($p > 0.05$). N/A: not applicable.

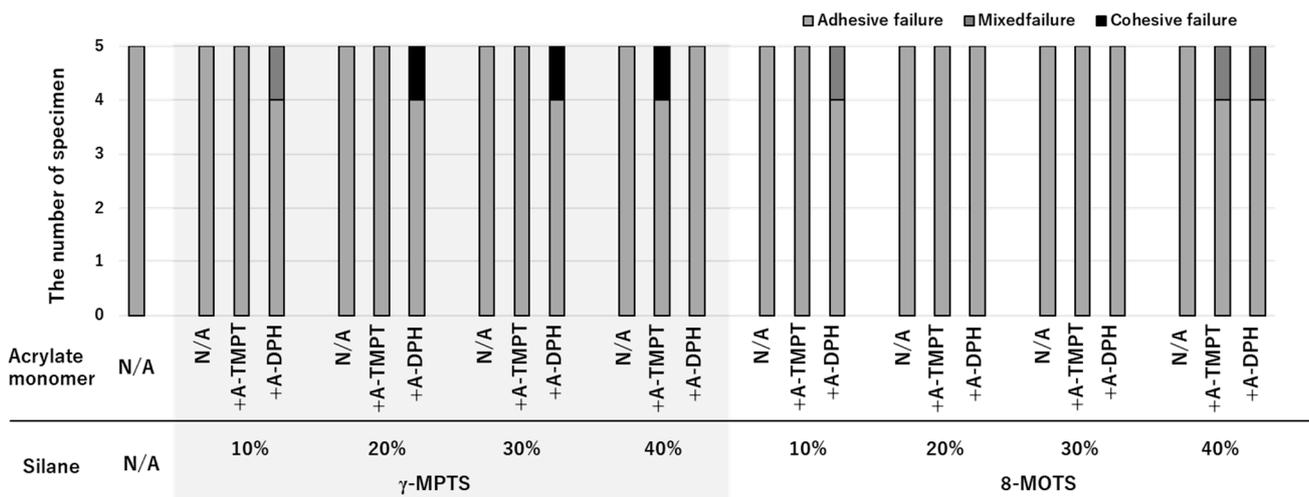


Figure 8. Distribution of failure modes after test. The gray area on the left side shows the results for γ -MPTS, and the right-sided white area shows the results for 8-MOTS. The horizontal axis shows the conditions for the silane coupling agent and acrylate monomer. N/A: not applicable.

Table 1. Shear bond strength value (MPa) and distribution of failure modes after test.

Silane		N/A	γ -MPTS 10%			γ -MPTS 20%			γ -MPTS 30%			γ -MPTS 40%		
Acrylate			N/A	TMPT	DPH									
Shear bond strength	Mean	2.4	6.1	4.5	14.0	3.5	5.5	19.0	6.6	9.1	15.8	4.1	6.0	14.6
	SD	2.0	1.1	1.7	4.5	2.0	3.3	7.0	0.7	5.4	5.1	0.4	2.7	2.3
Fracture mode	AF	5	5	5	4	5	5	4	5	5	4	5	4	5
	MF	0	0	0	1	0	0	0	0	0	0	0	0	0
	CF	0	0	0	0	0	0	1	0	0	1	0	1	0
Silane		N/A	8-MOTS 10%			8-MOTS 20%			8-MOTS 30%			8-MOTS 40%		
Acrylate			N/A	TMPT	DPH									
Shear bond strength	Mean	1.9	2.8	14.6	3.6	8.4	14.2	1.0	7.8	22.4	1.0	3.8	13.9	
	SD	3.0	1.9	5.6	1.3	4.1	1.6	2.1	3.7	6.1	2.0	3.8	4.1	
Fracture mode	AF	5	5	4	5	5	5	5	5	5	5	4	4	
	MF	0	0	1	0	0	0	0	0	0	0	1	1	
	CF	0	0	0	0	0	0	0	0	0	0	0	0	

AF: adhesive failure, MF: mixed failure, CF: cohesive failure, N/A: not applicable.

4. Discussion

This study sought to elucidate whether multifunctional acrylate monomers, when used with silane coupling agents—particularly those featuring alkyl chains—could synergistically enhance the adhesive strength of organic–inorganic nanohybrid dental materials. The observed improvement in shear bond strength between the material and luting resin cement, especially in formulations combining A-DPH with γ -MPTS or 8-MOTS, suggested a cooperative mechanism wherein silane-mediated chemical anchorage to filler surfaces was reinforced by a densely crosslinked acrylate network. Earlier studies have reported on the limited bonding efficacy of silane treatment alone. In contrast, this study showed that hybrid strategies were needed to achieve clinically durable bonding [5,24]. Indeed, the limited enhancement observed with silane agents alone aligned with literature, which claimed that silanization, while essential for forming covalent siloxane bonds upon inorganic fillers, often produced only moderate increases in bond strength [25].

γ -MPTS is widely used due to its efficient hydrolysis and methacrylate reactivity. It offers the highest bond ability on the condition that γ -MPTS forms a rigid monolayer upon the adhesive surface [26]. These limitations are frequently attributed to silane coupling agents' inability to adapt under oral conditions, which include temperature variations, high occlusal force and solubility. Compared to γ -MPTS, 8-MOTS—which bears a longer eight-carbon alkyl spacer—yielded lower shear bond strengths as a standalone treatment in this study. These results contrast with previous hypotheses that longer chains might improve toughness by increasing silane layer flexibility [8]. The decreased effectiveness observed here might result from its reduced hydrolytic reactivity and steric hindrance. Both of which might impair uniform silane film formation and inhibit strong filler surface bonding. This is because excessively long or hydrophobic silanes may easily form loosely bound or multilayered films that are mechanically weak and hydrolytically unstable. Therefore, while 8-MOTS offers theoretical advantages in stress modulation, its practical limitations in surface interaction reduce its standalone efficacy.

The incorporation of multifunctional acrylate monomers significantly improved bonding outcomes, whereby the extent of enhancement clearly depended on the monomer's degree of functionality. This was consistent with a previous work on multifunctional monomers [27], which demonstrated that monomers with higher numbers of reactive groups promoted more extensive crosslinking and led to stiffer, more durable interfacial polymer networks. A-TMPT, with three acrylate groups, showed only limited improvement. This reinforced earlier findings, which indicated that trifunctional monomers might lack the crosslink density required for substantial network reinforcement. In contrast, A-DPH, with six reactive acrylate groups, formed a highly interconnected network, significantly increas-

ing shear bond strength. Increase in functional group density could enhance the formation of interpenetrating polymer networks and reduce chain mobility, thereby improving both mechanical strength and hydrolytic resistance [28].

The combination of A-DPH and 8-MOTS, in particular, produced the most favorable results, with shear bond strength values surpassing all other formulations and a notable shift in failure mode from adhesive to cohesive. Cohesive failures are indicative of a well-integrated interface where interfacial bonding strength exceeds the internal strength of the materials. In this study, it was highly probable that the synergistic interaction between the flexible alkyl chain of 8-MOTS and the highly crosslinkable structure of A-DPH enabled simultaneous stress accommodation and chemical interlocking. The flexible silane layer provided better stress distribution under load, while the dense acrylate network formed by A-DPH contributed to mechanical reinforcement. These results endorsed the hybrid interface with further validation, in which mechanical compatibility and chemical bonding were co-optimized to enhance overall adhesive performance [29].

Notably, a detailed statistical interpretation of shear bond strength and failure modes provides strong quantitative support for these conclusions. The control group showed very low bond strength (2.4 ± 2.0 MPa) with 100% adhesive failure. Silane-only treatments produced moderate increases (e.g., 6.6 ± 0.8 MPa for 30% γ -MPTS and 3.6 ± 1.3 MPa for 20% 8-MOTS), but all failures remained adhesive. The addition of trifunctional A-TMPT slightly improved bond strength (e.g., 8.2 ± 1.5 MPa for γ -MPTS + A-TMPT), but differences were not statistically significant within silane groups. In contrast, incorporation of hexafunctional A-DPH significantly increased bond strength for all silane groups, with 30% 8-MOTS + A-DPH reaching 22.4 ± 6.1 MPa and 20% γ -MPTS + A-DPH reaching 19.0 ± 7.0 MPa. Tukey's post hoc tests confirmed these were significantly higher than both silane-only and A-TMPT-containing groups ($p < 0.05$), demonstrating a synergistic effect between high-functionality acrylates and silanes. A significant shift toward cohesive or mixed adhesive-cohesive failures in A-DPH groups ($p < 0.05$), with 50–60% of 30% 8-MOTS + A-DPH specimens failing cohesively. In contrast, control, silane-only, and A-TMPT groups showed 100% adhesive failures. This indicates that the interfacial bond strength in A-DPH groups confirmed the mechanical significance of the hybrid interface. Silane concentration and type also significantly influenced outcomes. Mid-range concentrations (20–30%) consistently outperformed low or high concentrations, confirmed by linear contrast analysis ($p < 0.01$). Excessive silane likely formed thick, weak multilayers, whereas low silane left unmodified filler sites. Interestingly, while 8-MOTS alone performed poorly, its combination with A-DPH produced the highest bond strengths, suggesting that the flexible alkyl chain facilitates stress distribution when embedded in a highly crosslinked network. Mixed adhesive-cohesive failures observed in some A-DPH specimens may reflect localized stress concentrations or incomplete monomer infiltration, emphasizing the importance of processing conditions.

Overall, the statistical analysis confirms that optimal bonding requires both a highly crosslinkable monomer (A-DPH) and a flexible, mid-range concentration silane (γ -MPTS or 8-MOTS). The correlation between shear bond strength and failure mode provides a robust metric for predicting clinical performance, quantitatively validating the synergistic mechanism of chemical anchorage, crosslinked network formation, and stress accommodation. These findings also warrant comparison with previously reported bonding strategies for the same material. The importance of silane concentration was also clearly demonstrated in this study. Mid-range concentrations (20–30%) consistently outperformed both lower and higher levels [30,31]. Excessive silane could result in thick, inhomogeneous multilayers prone to hydrolytic degradation and poor mechanical integration. At low concentrations, incomplete surface coverage could leave active filler sites unmodified, while high concen-

trations could promote condensation reactions that lead to weakly bonded multilayers. The present findings affirmed that precise silane dosing is critical—particularly with nanofillers whose high surface areas demand efficient but controlled surface modification.

To contextualize these findings, previous studies on the same organic–inorganic nanohybrid dental material investigated in this study, namely KATANA AVENCIA Block, have reported shear bond strength values of 29.52 ± 3.52 MPa when the surfaces were polished with 800-grit sandpaper prior to bonding [32]. In the present study, the surfaces were polished to a mirror finish using 2000-grit silicon carbide paper, without any additional mechanical pretreatment such as sandblasting or acid etching. Despite the absence of surface roughening, the combination of A-DPH and silane primers achieved a maximum shear bond strength of 22.4 ± 6.1 MPa. This comparison underscores that optimized chemical surface modification alone, through concentration-controlled multifunctional acrylate and silane coupling agents, can substantially enhance adhesion to this nanohybrid material.

On polymerization behavior, the superior performance of acrylate-based systems compared to methacrylates reflects the differences in their radical reactivity and polymerization kinetics. Acrylates, due to their lower steric hindrance and higher propagation rates, produce networks with higher crosslink densities and stiffer mechanical properties, which are better suited for reinforcing interfacial zones [33]. Acrylates may offer advantages over methacrylates in high-performance adhesive formulations, especially when fast curing and dimensional stability are desired. The effectiveness of A-DPH in this context suggests that its high functionality and acrylate structure may help overcome limitations of silane uniformity or suboptimal filler surface properties by forming a dominant, well-integrated polymer phase.

Although the results in this study were encouraging, several limitations must be acknowledged. This study focused solely on the immediate bond strength after 24 h of water storage. The oral environment subjects dental materials to long-term degradation due to moisture, enzymatic activity, temperature cycling, and mechanical fatigue [34]. In real-world clinical settings, these factors may substantially affect bond durability, which was not captured in the current study. Future studies should employ accelerated aging protocols—such as extended water immersion, thermocycling, and cyclic mechanical loading—to better simulate clinical conditions and assess long-term performance. Furthermore, surface characterization techniques such as XPS, FTIR, contact angle analysis and atomic force microscopy (AFM) would provide valuable insights into chemical bonding, surface energy changes, and topographical features resulting from different silane-acrylate combinations, because the surface chemical states correlate with mechanical adhesive performance. Comparing these results in more detail with previously reported bonding strategies, including mechanical pretreatments or different filler types, could help contextualize the clinical relevance of the chemical modification approach. The clinical applicability of the current formulations also warrants further study. While the primers used in this study were custom-prepared for experimental control, they might differ from commercial systems in terms of reactivity, initiator systems, and handling properties. Even small variations in monomer formulation or silane chemistry could impact curing behavior and biocompatibility. Future work should examine how multifunctional acrylate-silane systems perform with commercially available composites and luting cements, as well as evaluate potential cytotoxicity and practical usability in clinical workflows.

5. Conclusions

The present study offered mechanistic and empirical support for the strategic combination of flexible silanes and highly functional acrylate monomers to optimize resin-filler adhesion in nanohybrid dental materials. The observed synergy between 8-MOTS and

A-DPH provided compelling evidence that the simultaneous tuning of silane structure, concentration and monomer functionality could substantially enhance interfacial performance. These findings suggest that such concentration-controlled hybrid primers have the potential to improve the longevity and mechanical reliability of resin-based dental composites in clinical applications, although further long-term and biocompatibility studies are warranted to fully establish their clinical relevance.

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References

1. Toz-Akalin, T.; Öztürk-Bozkurt, F.; Kusdemir, M.; Özsoy, A.; Yüzbaşıoğlu, E.; Özcan, M. Three-year clinical performance of direct restorations using low-shrinkage Giomer vs. nano-hybrid resin composite. *Front. Dent. Med.* **2024**, *5*, 1459473. [[CrossRef](#)]
2. Liu, X.; Shum, W.W.-Y.; Tsoi, J.K.-H. Ultra-structural surface characteristics of dental silane monolayers. *Coatings* **2024**, *14*, 1005. [[CrossRef](#)]
3. Matinlinna, J.P.; Lung, C.Y.K.; Tsoi, J.K.H. Silane adhesion mechanism in dental applications and surface treatments: A review. *Dent. Mater.* **2018**, *34*, 13–28. [[CrossRef](#)] [[PubMed](#)]
4. Ozcan, M.; Matinlinna, J.P.; Vallittu, P.K.; Huysmans, M.C. Effect of drying time of 3-methacryloxypropyltrimethoxysilane on the shear bond strength of a composite resin to silica-coated base/noble alloys. *Dent. Mater.* **2004**, *20*, 586–590. [[CrossRef](#)]
5. Lung, C.Y.K.; Matinlinna, J.P. Aspects of silane coupling agents and surface conditioning in dentistry: An overview. *Dent. Mater.* **2012**, *28*, 467–477. [[CrossRef](#)]
6. 20Grob, B.; Wachter, N.; Liska, R.; Catel, Y. Heating of dental composites: The crucial role of the silane coupling agent on the consistency change. *Dent. Mater.* **2025**, *41*, 1131–1139. [[CrossRef](#)] [[PubMed](#)]
7. Awad, M.M.; Alhalabi, F.; Alanazi, A.A.; Alanazi, A.A.; Alshahrani, G.A.; Fu, C.; Albaijan, R.S.; Alkattan, R.; Fawzy, A.S. “No-Primer” Resin Cementation of Lithium Disilicate Ceramic: A Microtensile Bond Strength Evaluation. *Materials* **2023**, *17*, 137. [[CrossRef](#)]
8. Thadathil Varghese, J.; Cho, K.; Raju; Farrar, P.; Prentice, L.; Prusty, B.G. Influence of silane coupling agent on the mechanical performance of flowable fibre-reinforced dental composites. *Dent. Mater.* **2022**, *38*, 1173–1183. [[CrossRef](#)] [[PubMed](#)]
9. Fuchs, F.; Westerhove, S.M.; Schmohl, L.; Koenig, A.; Suharbiansah, R.S.R.; Hahnel, S.; Rauch, A. Influence of the Application Time of Silane for the Bonding Performance between Feldspar or Lithium Disilicate Ceramics and Luting Resin Composites. *J. Funct. Biomater.* **2023**, *14*, 231. [[CrossRef](#)]
10. Barghi, N.; Berry, T.; Chung, K. Effects of timing and heat treatment of silanated porcelain on the bond strength. *J. Oral Rehabil.* **2000**, *27*, 407–412. [[CrossRef](#)]
11. Hooshmand, T.; Matinlinna, J.P.; Keshvad, A.; Eskandarion, S.; Zamani, F. Bond strength of a dental leucite-based glass ceramic to a resin cement using different silane coupling agents. *J. Mech. Behav. Biomed. Mater.* **2013**, *17*, 327–332. [[CrossRef](#)]
12. Matinlinna, J.P.; Lassila, L.V.J.; Vallittu, P.K. Evaluation of five dental silanes on bonding a luting cement onto silica-coated titanium. *J. Dent.* **2006**, *34*, 721–726. [[CrossRef](#)]
13. Varghese, T.J.; Cho, K.; Raju; Farrar, P.; Prentice, L.; Prusty, B.G. Effect of silane coupling agent and concentration on fracture toughness and water sorption behaviour of fibre-reinforced dental composites. *Dent. Mater.* **2023**, *39*, 362–371. [[CrossRef](#)]
14. Fathy, H.; Hamama, H.H.; El-Wassefy, N.; Mahmoud, S.H. Effect of different surface treatments on resin-matrix CAD/CAM ceramics bonding to dentin: In vitro study. *BMC Oral Health* **2022**, *22*, 635. [[CrossRef](#)] [[PubMed](#)]
15. Tay, J.S.; Choong, B.B.L.; Ooi, I.H.; Tan, B.S. Effect of trifluoroethyl methacrylate comonomer on physical properties of Bis-GMA based dental composites. *Dent. Mater. J.* **2019**, *38*, 226–232. [[CrossRef](#)] [[PubMed](#)]

16. Leyva Del Rio, D.; Johnston, W.M. Optical characteristics of experimental dental composite resin materials. *J. Dent.* **2022**, *118*, 103949. [[CrossRef](#)]
17. Shi, S.; Nie, J. Investigation of 3,4-methylenedioxybenzene methoxyl methacrylate as coinitiator and comonomer for dental application. *J. Biomed. Mater. Res. B Appl. Biomater.* **2007**, *82*, 487–493. [[CrossRef](#)] [[PubMed](#)]
18. Fugolin, A.P.; de Paula, A.B.; Dobson, A.; Huynh, V.; Consani, R.; Ferracane, J.L.; Pfeifer, C.S. Alternative monomer for BisGMA-free resin composites formulations. *Dent. Mater.* **2020**, *36*, 884–892. [[CrossRef](#)]
19. Shobha, H.K.; Sankarapandian, M.; Sun, Y.; Kalachandra, S.; McGrath, J.E.; Taylor, D.F. Effect of dilution on the kinetics of cross-linking thermal polymerization of dental composite matrix resins. *J. Mater. Sci. Mater. Med.* **1997**, *8*, 583–586. [[CrossRef](#)]
20. Lee, T.Y.; Cramer, N.B.; Hoyle, C.E.; Stansbury, J.W.; Bowman, C.N. (Meth)acrylate vinyl ester hybrid polymerizations. *J. Polym. Sci. A Polym. Chem.* **2009**, *47*, 2509–2517. [[CrossRef](#)]
21. Miyazaki, K.; Horibe, T. Polymerization of multifunctional methacrylates and acrylates. *J. Biomed. Mater. Res.* **1988**, *22*, 1011–1022. [[CrossRef](#)]
22. Matinlinna, J.; Ozcan, M.; Lassila, L.; Kalk, W.; Vallittu, P. Effect of the cross-linking silane concentration in a novel silane system on bonding resin-composite cement. *Acta Odontol. Scand.* **2008**, *66*, 250–255. [[CrossRef](#)]
23. Mendes, L.T.; Loomans, B.A.C.; Opdam, N.J.M.; Silva, C.L.D.; Casagrande, L.; Lenzi, T.L. Silane coupling agents are beneficial for resin composite repair: A systematic review and meta-analysis of in vitro studies. *J. Adhes. Dent.* **2020**, *22*, 123–137.
24. Matinlinna, J.P.; Vallittu, P.K. Bonding of resin composites to etchable ceramic surfaces—An insight review of the chemical aspects on surface conditioning. *J. Oral Rehabil.* **2007**, *34*, 622–630. [[CrossRef](#)] [[PubMed](#)]
25. Mao, Z.; Schmidt, F.; Beuer, F.; Yassine, J.; Hey, J.; Prause, E. Effect of surface treatment strategies on bond strength of additively and subtractively manufactured hybrid materials for permanent crowns. *Clin. Oral Investig.* **2024**, *28*, 371. [[CrossRef](#)] [[PubMed](#)]
26. Liu, Q.; Ding, J.; Chambers, D.E.; Debnath, S.; Wunder, S.L.; Baran, G.R. Filler-coupling agent-matrix interactions in silica/polymethylmethacrylate composites. *J. Biomed. Mater. Res.* **2001**, *57*, 384–393. [[CrossRef](#)]
27. Ferracane, J.L. Hygroscopic and hydrolytic effects in dental polymer networks. *Dent. Mater.* **2006**, *22*, 211–222. [[CrossRef](#)]
28. Moszner, N.; Salz, U. New developments of polymeric dental composites. *Prog. Polym. Sci.* **2001**, *26*, 535–576. [[CrossRef](#)]
29. Oilo, G. Bond strength testing—what does it mean? *Int. Dent. J.* **1993**, *43*, 492–498. [[PubMed](#)]
30. Matinlinna, J.P.; Lassila, L.V.J.; Ozcan, M.; Yli-Urpo, A.; Vallittu, P.K. An introduction to silanes and their clinical applications in dentistry. *Int. J. Prosthodont.* **2004**, *17*, 155–164.
31. Piascik, J.R.; Wolter, S.D.; Stoner, B.R. Development of a novel surface modification for improved bonding to zirconia. *Dent. Mater.* **2011**, *27*, e99–e105. [[CrossRef](#)] [[PubMed](#)]
32. Fouquet, V.; Lachard, F.; Abdel-Gawad, S.; Dursun, E.; Attal, J.P.; François, P. Shear Bond Strength of a Direct Resin Composite to CAD-CAM Composite Blocks: Relative Contribution of Micromechanical and Chemical Block Surface Treatment. *Materials* **2022**, *15*, 5018. [[CrossRef](#)] [[PubMed](#)]
33. Bygott, E.G.; Pahovnik, D.; Žagar, E.; Hutchinson, R.A. The Synthesis of Acrylate-Based Macromonomers and Structured Copolymers by High-Temperature Semi-Batch Radical Polymerization: The Impact of Acrylate vs. Methacrylate Monomer Choice. *J. Polym. Sci.* **2025**, *63*, 1717–1726. [[CrossRef](#)]
34. De Munck, J.; Van Landuyt, K.; Peumans, M.; Poitevin, A.; Lambrechts, P.; Braem, M.; Van Meerbeek, B. A critical review of the durability of adhesion to tooth tissue: Methods and results. *J. Dent. Res.* **2005**, *84*, 118–132. [[CrossRef](#)]

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