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Effect of solvent pretreatments on intraradicular bond strength of bioactive cements

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ABSTRACT

Bioactive materials are gaining interest in dentistry due to their ability to interact with dental tissues promoting healing and regeneration; albeit their ability to bond to root dentin remains unclear. This study investigated the effect of solvent-containing pretreatments on intraradicular bond strengths of bioactive cements. Sound premolars were decoronated, root canals were instrumented and irrigated using sodium hypochlorite and water. Roots were randomly divided into eighteen groups (n = 7/group) based on dentin pretreatments (no treatment, dimethyl sulfoxide (DMSO), ethanol (EtOH), EtOH/H_2O, DMSO/H_2O and DMSO/EtOH) and bioactive cements; a light-curable calcium silicate (Theracal LC, Bisco, Chicago, Illinois, USA), a mineral trioxide aggregate (Orbis MTA, P.L. Superior Dental Materials GmbH, Hamburg, Germany), and an experimental surface pre-reacted glass ionomer root canal material (S-PRG, Shofu Inc, Higashiyama-ku, Kyoto, Japan). Root canals were filled with bioactive cements and stored for 7 days at 37 °C. Filled roots were sectioned perpendicular to their longitudinal axis to obtain 1-mm thick slices. Intraradicular bond strengths were measured by the push-out bond strength test (0.5 mm/min). Analysis of failure mode was performed using a stereomicroscope. Characterization of bonded interfaces was performed via SEM. Bond strength data was analyzed by Kruskal Wallis test and ANOVA on ranks ($\alpha = 0.05$). Bond strengths varied according to bioactive cements, Theracal > MTA > S-PRG, and root thirds ($p < 0.05$). Aqueous (DMSO/H_2O) or ethanolic (DMSO/EtOH) dilutions of DMSO increased Theracal bond strengths to apical root segments ($p < 0.05$). While MTA bond strengths were not affected by pretreatments, undiluted ethanol reduced bond strengths of S-PRG to apical root segments ($p < 0.05$). Intraradicular bonding of bioactive cements may vary according to root canal depth and material composition. Solvent-based pretreatments containing DMSO might improve intraradicular bonding of resin-modified bioactive cements in a concentration-dependent manner.

1. Introduction

In endodontics, an ideal filling material must bond to dentin and seal the communication pathway of the root from its surrounding tissue [1,2]. In addition, the filling material should meet certain criteria including biocompatibility, leakage prevention, optimal adaptation to the tooth structure, and high bond strength against dislodging movement, especially in cases of perforation [3]. Moreover, the material should have the ability to chemically interact with the living tissues of the body which is known as the bioactivity, this ability results from the release of ion that led to the formation of a mineralized layer on he surface of the material [4]. Calcium-silicate materials offer excellent sealing properties. In addition, they can stimulate the formation of apatite-like precipitates when they react with phosphate-containing liquids. This reaction releases ions that promote the growth of dentin bridges [5]. Multiple calcium silicate-based materials, particularly mineral trioxide aggregate (MTA), have been

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developed with those goals in mind due to their biocompatibility [6], sealing ability [7], regenerative capabilities [8], and antibacterial activity [9]. However, MTA's handling difficulties [10,11], and prolonged setting time [12] pose practical challenges for clinical applications [13].

Resin-modified calcium silicate-based cements (RMCS) were introduced to address these drawbacks by combining calcium-silicate materials properties with enhanced handling through a resin-based matrix [14]. Apart from its easy handling and precise placement characteristics, RMCS has demonstrated effective sealing capability, reduced interfacial microleakage, lower solubility, and increased release of calcium ions compared to MTA and Dycal [15,16]. It also enables immediate placement of the final restorative material, eliminating the need for a waiting period required by other calcium-silicate cements. A new emerging bioactive material, surface pre-reacted glass ionomer fillers (S-PRG), are known for their ion-releasing properties [17]. S-PRG fillers are employed in various dental applications, including composite resins [18], fissure sealants [19], and tooth coating materials [20], due to their antibacterial activity [18], acid buffering capacity [18,21], and multiple ion releasing ability [21–23]. Although several studies evaluated the physical and mechanical properties of the S-PRG fillers, the bonding ability of the S-PRG cement to root dentin remains unclear.

Previous studies have shown that the use of aqueous DMSO solutions can improve both immediate and long-term bond strengths of resin-based materials to dentin [24–26]. DMSO preserves bond strengths [27,28] by improving resin penetration and monomer diffusion into the collagen matrix [29]. Ethanol is another solvent that was suggested to control dentin moisture and enhance bond strength [30]. Several previous studies evaluated the effect of solvent pretreatments containing DMSO, ethanol or their combinations on dentin bonding [27,31,32]. However, the effect of these pretreatments on bonding of bioactive materials to root dentin remains inconclusive. Getting a good adhesion of the materials in the root canal is difficult due to its complex structure. The dentin in the middle third of the root has a higher density of dentinal tubules with a greater diameter than that in the apical third [33], the bond strength measurement of bioactive cements is important to enable the quantification of the dentin/material interaction. Therefore, the aim of this study was to assess the effect of solvent-containing pretreatments (DMSO, ethanol, and their aqueous dilutions) on the push-out bond strength of different bioactive cements. The tested null hypotheses were that; (i) the different compositions of the bioactive cements or (ii) the type of root canal pretreatments (DMSO, ethanol, or their aqueous dilutions) before bioactive cement application does not significantly affect the intraradicular push-out bond strength or interfacial integrity.

2. Materials and methods

2.1. Teeth selection and root canal preparation

One hundred twenty-six sound premolars with completely formed apex, collected from anonymous donors, and exempt from ethical notification, were obtained following local regulations (Tissue Act, section 20) were collected. Teeth were stored in 0.9 % NaCl supplemented with 0.02 % sodium azide at 4 °C until use. Teeth with calcified canals, cracks or fractures, developmental defects, multiple canals, and root caries were excluded. All teeth were horizontally decoronated at the level of 0.5 mm radicular to the cemento-enamel (CE) junction using a 0.3-mm-thick, diamond-coated slow-speed band saw (Buehler Ltd., Lake Bluff, IL, USA) generating 16 mm (±1 mm) long roots. Apical patency was verified using an ISO size-10 K-file (Dentsply Maillefer, Ballaigues, Switzerland). The working length of each root was determined by visualizing the tip of a size 10 K file extending beyond the apical foramen and subtracting 1 mm from that length of the file. Canals were instrumented using rotary nickel-titanium instruments (Protaper SX, S1, S2, F1, F2, F3, F4; Dentsply Maillefer) using a low-speed rotary endodontic handpiece (X-smart; Dentsply Maillefer). The master apical instrument was the Protaper F4. Carbide fiber post preparation burs (3M ESPE RelyX, St. Paul, USA) up to size #3 (1.9 mm in diameter) were used at low speed to standardize the canal diameter. Irrigation was performed using 27-G Endo-Eze irrigator tips (Ultradent Products Inc, South Jordan, UT) alternating 2 mL 2.5 % sodium hypochlorite and Glyde File Prep (Dentsply Maillefer, Ballaigues, Switzerland) between the use of each instrument and at the end of instrumentation with 2 mL 17 % EDTA (Inter-Med Inc/Vista Dental Products, Racine, WI) for 1 min, followed by 2 mL normal saline. The root canals were dried with 2 paper points size F4 (Dentsply, York, PA, USA). Roots were then randomly divided into eighteen groups (n = 7/group) according to the bioactive cement used and the pretreatment.

2.2. Preparation of pretreatment solutions

A total of five dentin pretreatment solutions were prepared and stored at room temperature until use, containing dimethyl sulfoxide (DMSO, Dimethyl sulfoxide, Sigma-Aldrich, St. Louis, MO, USA) and/or ethanol (Ethanol 99.8 %, Sigma-Aldrich). The concentrations (v/v) of the solvents were as follows: pure ethanol (EtOH), pure dimethyl sulfoxide (DMSO), 50 % aqueous ethanol (EtOH/H2O), 50 % aqueous dimethyl sulfoxide (DMSO/H2O), and 50 % ethanolic dimethyl sulfoxide (DMSO/EtOH) [34].

2.3. Experimental design and root filling

The experimental design was composed of two study factors: (i) dentin pretreatment at six levels (no pretreatment; ethanol; dimethyl sulfoxide; 50 % aqueous ethanol; 50 % aqueous dimethyl sulfoxide; 50 % ethanolic dimethyl sulfoxide) and (ii) bioactive cements at three levels (light-curable resin-modified calcium silicate; mineral trioxide aggregate, and an experimental surface pre-reacted glass ionomer). A total of 18 experimental groups were obtained (n = 7 roots/group). The composition of test materials and application procedures are shown in Table 1, while a flowchart outlining the experimental design is presented in Fig. 1. A light-curable calcium silicate (Theracal LC, Bisco, Chicago, Illinois, USA), a mineral trioxide aggregate (Orbis MTA, P.L. Superior Dental Materials GmbH, Hamburg, Germany), and an experimental surface pre-reacted glass ionomer root canal material (S-PRG,

Table 1
Composition of calcium silicate biomaterials and application procedures.

	Composition	Application procedure
Resin-modified calcium silicate-based cement. Theracal L.C, Bisco Inc, Schamburg, IL, USA	Light cured resin-modified calcium silicate. Tricalcium silicate particles in a hydrophilic monomer.	The material comes in a premixed syringe, apply a 2 mm thick layer inside the canal and light cure for 20 s using a light curing unit (Elipar; 3M ESPE) at 1200 mW/cm^2
Mineral Trioxide Aggregate Orbis MTA, P.L. Superior Dental Materials GmbH, Hamburg, Germany	Di- and Tricalcium silicate and Tricalciumaluminate Portland Cement Clinker, and bismuth oxide	Mix 1 full spoon present in the kit with 2 drops of the liquid present in the kit. Increments of the material were placed inside the canals using amalgam carrier and a plugger, to ensure the whole canal's filling. A wet cotton plate was placed over the MTA.
Surface pre-reacted glass (S-PRG) Shofu Inc, Higashiyama-ku, Kyoto, Japan	Fluoro-boro- aluminosilicate core glass, pre-reacted glass-ionomer phase, SiO_2. Ion release: Al^{3+}, BO_3^{3-}, Na^{+}, SiO_2^{3-}, Sr^{2+} and F^{-}.	Mix 2.8 g powder with 1 g liquid, increments of the material were placed inside the canal using an amalgam carrier and a plugger to ensure the filling of the whole canal.

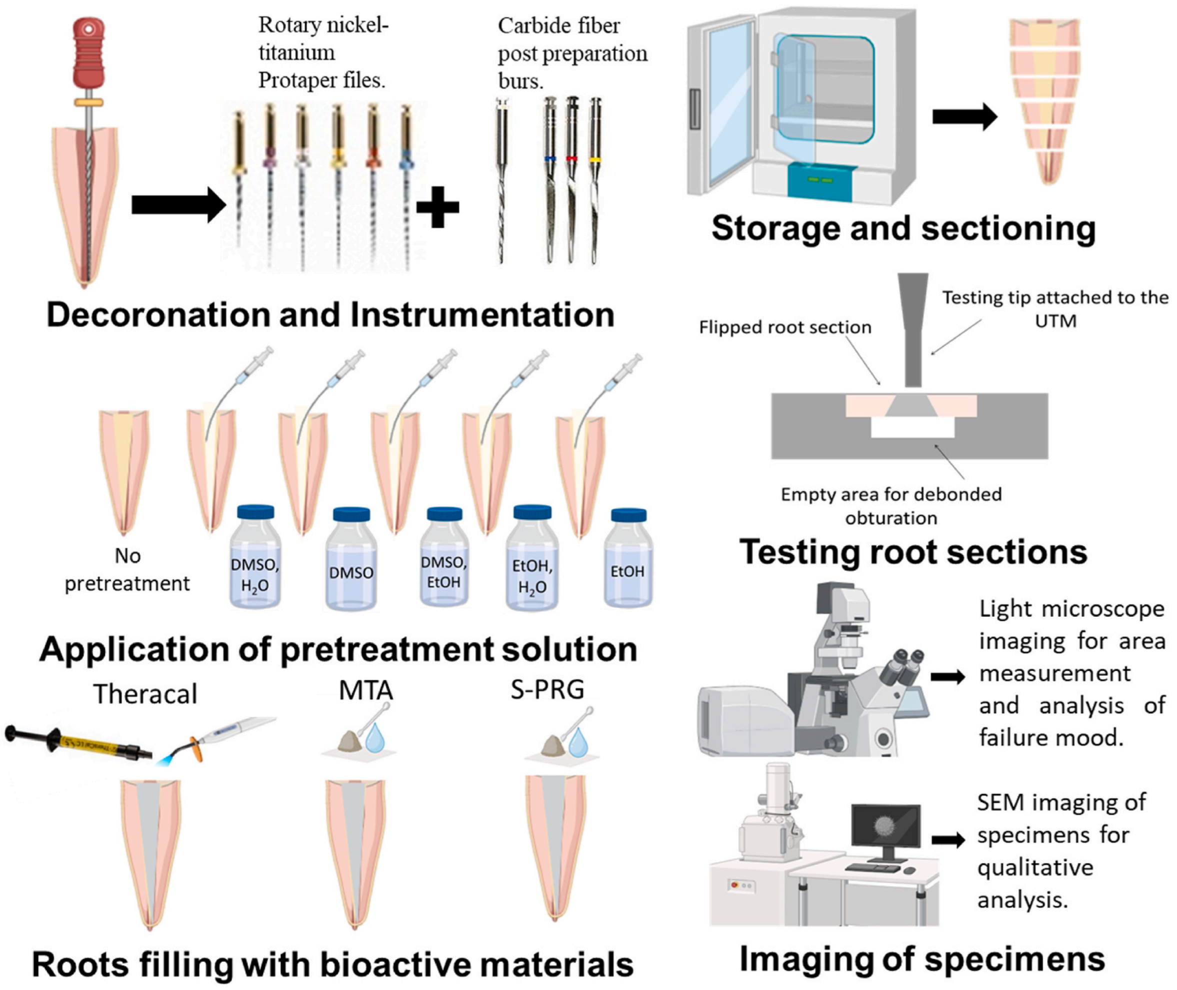

Fig. 1. Flowchart of the experimental design and scheme of testing used for push-out evaluation.

Shofu Inc, Higashiyama-ku, Kyoto, Japan) were used following manufacturer's instructions.

Root fillings were performed by a single operator. One ml of the tested pretreatment solution was applied inside the canal using a tuberculin syringe with a 30-G blunt-tip needle, carried to the working length, and gently injected into the root canal while slowly withdrawing the syringe. Flooding of the pretreatment solution was visually verified and left in the canal for 60 s. The excess pretreatment solutions were removed with paper points, followed by the placement of the filling bioactive material. MTA and S-PRG were mixed according to the manufacturers' instructions and manually plugged into the root canals in their respective groups using hand pluggers. Untreated roots served as control. Roots were kept at 100 % relative humidity and stored at 37 °C for 7 days to allow complete setting of MTA. Following the storage period, each root was sectioned horizontally perpendicular to the longitudinal axis using a low-speed diamond-coated saw (Isomet 2000, Buehler Ltd, Lake Bluff, IL, USA) under water cooling at three different levels (namely: coronal, middle, and apical) to obtain 6 slices of 1 ± 0.1 mm in thickness. The thickness of each root cylinder was measured to the nearest 0.01 mm using a digital caliper.

2.4. Push-out bond strength testing

The push-out technique was performed by applying a load using a universal testing machine (AGS-10, Shimadzu Corp., Kyoto, Japan), each specimen was subjected to a compressive loading apico-coronally at a crosshead speed of 1 mm/min until failure and the maximum load was recorded in newton (N). After taking images of the specimens using a stereomicroscope (Leica M165C, Leica Microsystems GmbH., Wetzlar, Germany) with 20x magnification. The smaller and larger root canal diameters were measured using digital image-analysis software (ImageJ; National Institute of Health, Bethesda, Maryland, USA). The adhesion surface area was calculated in the same way as measuring the area of a trapezium following the equation: adhesion surface area (mm^2) = ((D1 + D2)/2) πh where D1 and D2 are the largest and smallest canal diameter, respectively, π is the constant 3.14, and h is the thickness of the root slice [35,36]. To obtain the push-out bond strength in mega Pascal (MPa), the load (N) at failure was divided by the surface area (mm^2) of the root canal at the filling-dentin interface.

2.5. Analysis of failure modes

The failure modes were analyzed under a stereomicroscope at 40x magnification. Failure modes were categorized as follows: adhesive (failure at the cement-dentin or the sealer-core material interface), cohesive (failure within bioactive cement or dentin), or mixed (failure in both the cement and dentin) [37].

2.6. Characterization of bonded interfaces (SEM)

Qualitative analysis of the interface between dentin and bioactive cement was performed using SEM imaging. Representative discs from each group were embedded in epoxy resin and wet-polished with 600, 1200, 2000, and 4000-grit SiC paper, followed by 0.05 μm aluminum oxide polishing paste (Buehler Ltd, USA). Beams were ultrasonically cleaned in distilled water for 10 min after each polishing step. Bonded interfaces were treated with 50 % H_3PO_4 for 5 s and 3 % NaOCl for 10 min, dried in silica overnight, mounted on stubs, and analyzed on backscattering mode at 15 kV (Phenom ProX, Phenom-World, USA [31, 34]. A series of sequential micrographs of the bonded interfaces (2000 × magnification) were obtained from each resin-dentin beam by an experienced blinded operator. Sequential micrographs (2000 magnification) were obtained from all groups to analyze the interface.

3. Statistical analysis

Push-out bond strength values for all tested groups were analyzed using IBM SPSS Statistics for Windows, version 26 (IBM Corp., Armonk, NY, USA). Both root segments and whole root data were evaluated and failed in normality and homoscedasticity testing ($p < 0.05$). Kruskal Wallis test and ANOVA on ranks for pair-wise comparisons were performed with statistical significance set at $\alpha = 0.05$.

4. Results

4.1. Push-out bond strength

The results of the push-out bond strengths are shown in Fig. 2. Material-wise, the control group where Theracal was used without the application of any pretreatment showed significantly higher bond strengths (29.1 MPa) compared to the control MTA (17.88 MPa) or the control S-PRG (7.22 MPa) bond strength value ($p < 0.05$). None of the pretreatments significantly affected the intraradicular bond strengths of the bioactive cements ($p > 0.05$).

4.2. Push-out bond strength at different root thirds

Push-out bond strengths of the tested materials at different root thirds (coronal, middle, and apical) are shown in Table 2. Intraradicular bond strengths of bioactive cements varied according to root third and dentin pretreatments ($p < 0.05$). For Theracal, intraradicular bond strengths were higher at the coronal third compared to the apical third in all groups except for the DMSO/H2O and DMSO/EtOH treated groups ($p < 0.05$). DMSO pretreatment produced lower intraradicular bond strengths of Theracal at the apical third compared to the apical third of the control group ($p < 0.05$). Dentin pretreatments had no significant effects on bond strengths of Theracal to coronal or middle root thirds ($p < 0.05$).

For MTA, no significant differences were seen between root thirds (coronal, middle, or apical) within dentin pretreatments, except for EtOH ($p < 0.05$). EtOH caused significant bond strength reductions at the apical third ($p < 0.05$). Dentin pretreatments produced comparable intraradicular bond strengths within root thirds ($p > 0.05$).

For S-PRG, intraradicular bond strengths were generally lower than Theracal and MTA ($p < 0.05$). Intraradicular bond strengths at apical thirds were significantly lower than coronal thirds, regardless of dentin pretreatments ($p < 0.05$). Dentin pretreatments had no effects within root thirds except for the DMSO-treated group which caused a reduction in the bond strength of the middle and apical third compared to control ($p < 0.05$).

4.3. Analysis of failure modes

Failure modes for all tested materials are shown in Fig. 3. Generally, in all tested groups, the least seen failure mode was the adhesive failure. Mixed failures were the most common failure mode for Theracal at around 50 % for all pretreatments except for the ethanol-treated group (EtOH), where cohesive failure was found in 95 % of specimens, with failure occurring within the Theracal. A different trend was seen in the MTA groups where the most commonly seen failure mode was mixed failure with more than 60 % for groups where ethanol was used at its different dilutions, when DMSO was used as a pretreatment, both adhesive and cohesive failure within the material were recorded at a similar percentage of around 48 %. The S-PRG groups consistently failed within the material, as indicated by the percentage of cohesive failures (more than 40 % with all pretreatments). The control group exhibited a

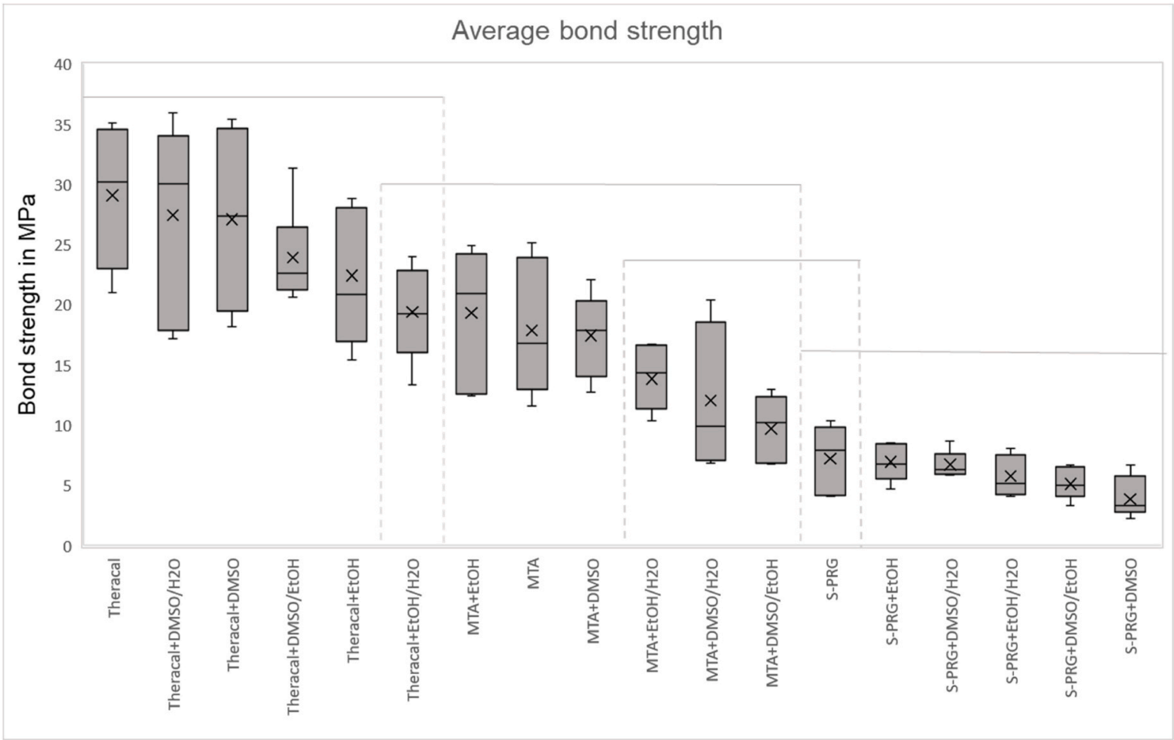

Fig. 2. Push-out bond strength value in mega Pascal for the different tested silicate-based materials.

Table 2
Means and standard deviations (±) of push-out bond strengths (MPa) at different root thirds.

	Theracal			MTA			S-PRG		
	Coronal	Middle	Apical	Coronal	Middle	Apical	Coronal	Middle	Apical
Control	$31.46^{Aa}\pm10.49$	$25.45^{Aab}\pm9.22$	$20.52^{Ab}\pm8.97$	$20.12^{Aa}\pm11.9$	$21.88^{Aa}\pm10.21$	$12.08^{Aa}\pm4.81$	$8.10^{Aa}\pm3.25$	$8.59^{Aa}\pm3.22$	$4.18^{ABb}\pm1.98$
DMSO/H_2O	$27.81^{Aa}\pm10.32$	$28.38^{Aa}\pm11.16$	$22.27^{ABa}\pm6.7$	$12.16^{Aa}\pm5.82$	$13.57^{Aa}\pm7.13$	$11.61^{Aa}\pm3.11$	$7.44^{Aa}\pm2.01$	$6.66^{ABab}\pm3.02$	$4.96^{Ab}\pm2.24$
DMSO	$28.71^{Aa}\pm8.52$	$25.54^{Aa}\pm8.69$	$14.82^{Bb}\pm5.12$	$17.78^{Aa}\pm4.20$	$17.62^{Aa}\pm5.31$	$17.39^{Aa}\pm5.57$	$5.36^{Aa}\pm3.55$	$4.33^{Bab}\pm1.51$	$2.99^{Bb}\pm1.07$
DMSO/ EtOH	$25.75^{Aa}\pm8.91$	$25.45^{Aa}\pm12.81$	$22.14^{Aa}\pm7.31$	$11.70^{Aa}\pm6.81$	$15.78^{Aa}\pm7.01$	$13.80^{Aa}\pm6.45$	$7.11^{Aa}\pm2.84$	$6.11^{Aa}\pm1.05$	$3.82^{Ab}\pm1.02$
EtOH/H_2O	$27.92^{Aa}\pm15.06$	$26.80^{Aa}\pm9.58$	$18.02^{ABb}\pm6.02$	$13.73^{Aa}\pm5.72$	$15.38^{Aa}\pm5.20$	$11.61^{Aa}\pm5.37$	$7.71^{Aa}\pm3.34$	$6.28^{ABa}\pm3.21$	$3.79^{Ab}\pm0.92$
EtOH	$30.06^{Aa}\pm9.29$	$26.08^{Aa}\pm4.81$	$22.39^{Ab}\pm4.41$	$18.55^{Aa}\pm11.34$	$19.99^{Aa}\pm9.30$	$12.39^{Ab}\pm8.81$	$8.40^{Aa}\pm4.31$	$8.91^{Aab}\pm1.23$	$4.56^{Ab}\pm1.81$

Different capital letters represent significant differences between different pretreatments within the root third (column) for each silicate-based material according to ANOVA on ranks ($p < 0.05$). Different lowercase letters represent significant differences between root thirds within dentin pretreatments (row) for each silicate-based material according to ANOVA on ranks ($p < 0.05$).

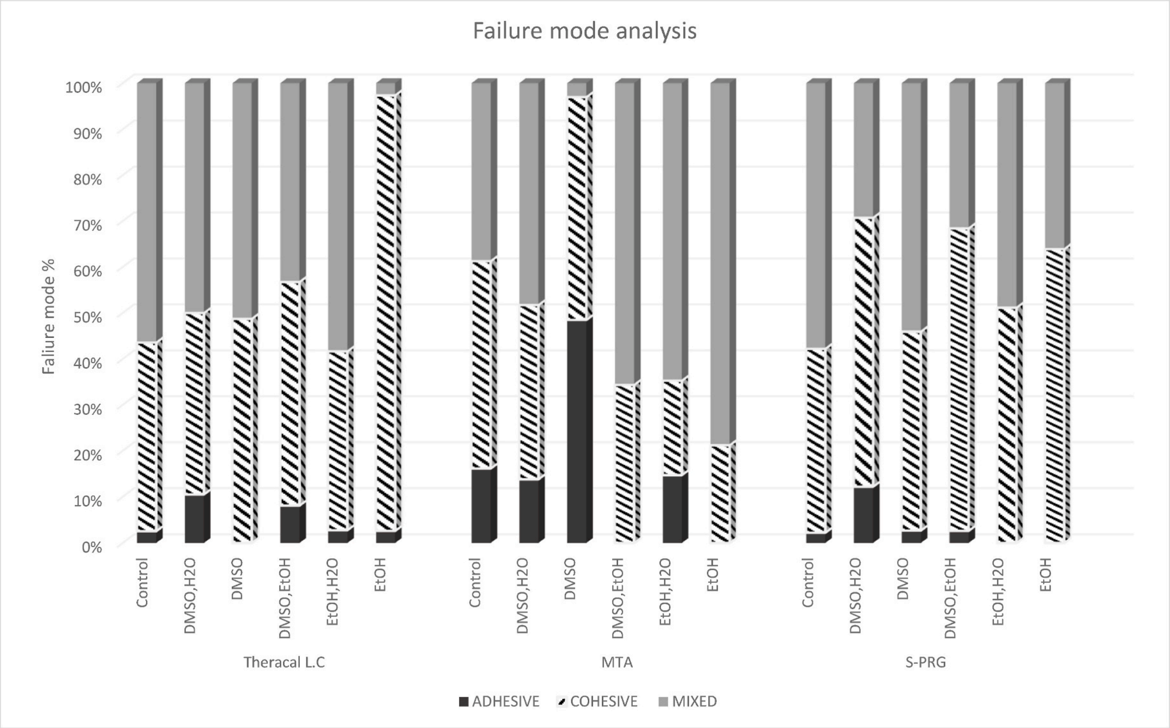

Fig. 3. Push-out fracture mode percentages in different groups.

combination of cohesive and mixed failures, with mixed failure occurring in more than 57 % of the specimens.

4.4. Characterization of bonded interfaces (SEM)

Representative scanning electron microscopic images of all tested materials and pretreatments are shown in Fig. 4. A clear penetration of the Theracal into the dentinal tubules was seen in the control group, DMSO diluted in water (DMSO/H2O), and DMSO treated group (DMSO). Smaller tags were seen at the bonded interface between the Theracal and dentin for ethanol-treated groups. MTA showed the deepest penetration in the group with ethanol and the control group where no pretreatment was applied. Small tags or accumulations of the material on the dentin-material margin were seen in all other treated groups. In the experimental S-PRG groups, little to no penetration was observed.

5. Discussion

Since the composition of bioactive cements affected intraradicular bond strengths, the first null hypothesis was rejected. The rationale for employing the push-out test was to verify whether variations of dentin morphology inside root canals (cervical, middle, or apical thirds) could affect the bonding performance of silicate-based materials. The push-out setup is a commonly used method to test intraradicular bond strengths [38]. It is the most reliable mechanical test to rank the dislodgement resistance of various endodontic materials applied to root dentin such as root canal sealers, root repair materials, and intraradicular posts [39]. There were significant differences in intraradicular bond strengths between the tested bioactive cements when root thirds were polled together: Theracal > MTA > S-PRG ($p < 0.05$). Theracal's higher bond strengths can be attributed to the presence of methacrylate-based hydrophilic monomers, which can improve their penetration into dentinal tubules, enhancing bond strengths [40]. In addition, previous

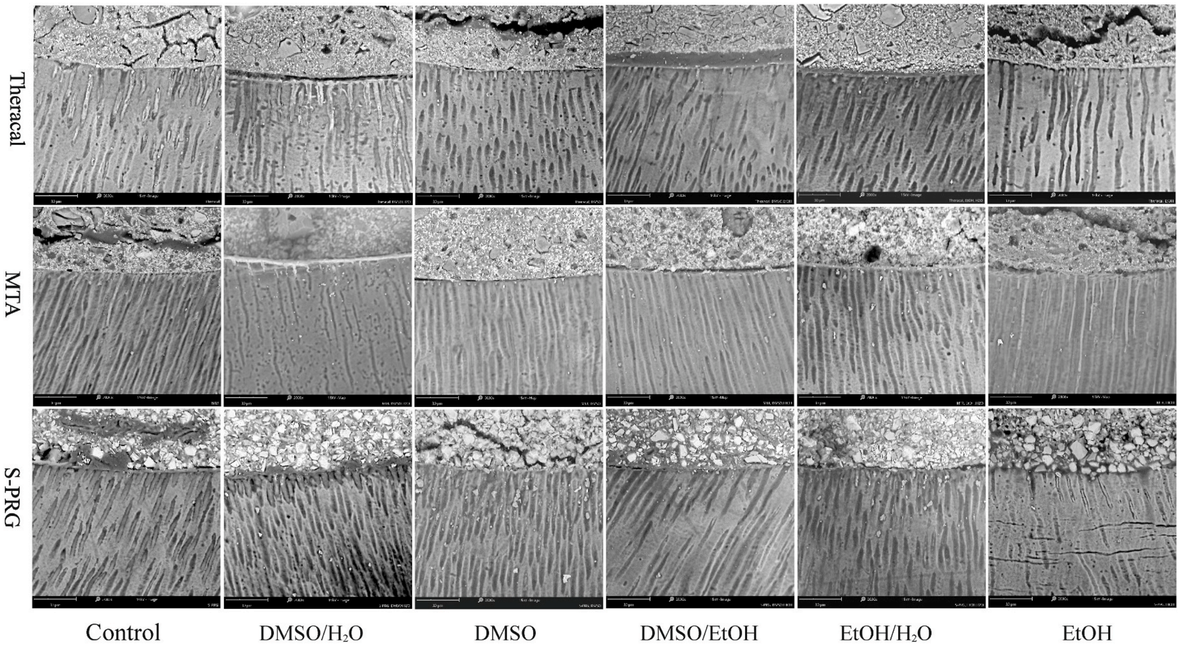

Fig. 4. Representative SEM images of the different tested materials and pretreatments.

reports [36] corroborate the obtained higher bond strengths of MTA compared to S-PRG. This may be related to the biomineralization abilities [41] and the relatively fast expansion of MTA [42]. The low bond strengths of S-PRG cement could be related to the short storage period (7 days) in this study. This period was chosen to comply with the most commonly used storage time to evaluate the bond strengths of silicate-based cements [35,43]. Additionally, ion release from S-PRG including fluoride, strontium, and silicon was suggested to incorporate deeper into root dentin only after 1–3 months of application [44]. Relatively longer storage times may contribute to better bonding outcomes for S-PRG [36,44].

Not only did bond strengths vary among bioactive cements, but the depth inside root canals also affected bonding efficiency. While Theracal and S-PRG presented significant reductions in bond strengths at the apical third, MTA was not affected by changes in dentin morphology inside root canals ($p < 0.05$). Theracal is a light-curable resin-based cement. The increased distance between the light source and the apical region leads to a lower conversion of methacrylate monomers, thereby compromising intraradicular bonding. This is in agreement with previous reports [45], which corroborate the lower bond strengths in the apical third compared to the coronal third for Theracal. In addition, the significant differences in dentinal tubule density between the coronal third and apical third [46,47], the orientation of the tubules [46], and the degree of tubular sclerosis [48] between apical and coronal thirds of the roots may be attributed to the significant change of the bond strength in the apical third. Surface pre-reacted glass ionomer fillers (S-PRG) were introduced as bioactive materials that retain their basic properties by forming a stable glass ionomer phase on the treated surface through the acid-base reaction between the fluoro-boro-alumino-silicate glass and polyacrylic acid [21]. Although the S-PRG formulation used in this study did not incorporate light-curable components, bond strengths were still lower at the apical region. This is not in agreement with a previous report showing no differences between root segments [36]. In the present study, S-PRG-tag formation in the apical third was not easily identified at bonded interfaces given the relatively large S-PRG filler sizes. The filler size easily exceeds the cross-sectional area of dentin tubules at the apical region. Additionally, the paste-like consistency of the tested experimental S-PRG cement may have prevented optimum tag formation. Since dentinal tubule density and size decrease at the apical third, S-PRG retention was likely compromised resulting in lower bond strengths. Differently, MTA showed no changes in intraradicular bond strengths among root segments. This is in agreement with previous studies [35,36]. MTA-based materials bond by the deposition of hydroxyapatite which causes the formation of a mineral infiltration zone with a tag-like structure at the interface with the dentin [49,50]. The tested MTA was a resin-free version, not relying on light curing for setting, but rather depending only on the slow hydration reaction of the hydrophilic MTA particles [51]. MTA-tag formation at the apical third was easily identified at bonded MTA-dentin interfaces, showing MTA's capacity to penetrate dentinal tubules.

The reason for combining bioactive cements and solvent pretreatments was to benefit from the solvents' ability to improve material-dentin interactions. Solvents, such as DMSO, can increase dentin wettability [34], which is a primary requirement for good adhesion. Recent studies have shown that even low concentrations of DMSO can improve immediate and long-term bond strengths of resin-based materials to coronal dentin [24–26]. DMSO concentrations were chosen based on previous studies [24,29,52] showing that the use of relatively higher DMSO concentrations (50 % v/v) substantially improves interactions between resin-based materials and dentin. Since the effect of solvents used as dentin pretreatments on intraradicular bond strengths of bioactive cements depended not only on cement composition but also on the solvent type and dilution, the second null hypothesis was rejected. The most promising effects were obtained for Theracal combined with diluted DMSO pretreatments. DMSO/H2O and DMSO/EtOH were able to increase the bond strengths of Theracal on the apical third, producing comparable bond strengths to coronal or middle thirds. DMSO can increase monomer conversion at resin-dentin interfaces [52] and lower the termination rates in free radical polymerization of methacrylates [53], likely improving polymer formation of Theracal on such challenging root segments [46]. Interestingly, bond strength improvements for Theracal were only observed for the apical third even though pretreatments were similarly applied in all root segments. Future studies must evaluate the sealing ability of pretreated dentin bonded with bioactive cements to investigate potential improvements that were not reflected as higher bond strengths. It is important to note that undiluted DMSO reduced bond strengths at the apical third for Theracal. Undiluted DMSO has a low vapor pressure. Unlike ethanol, it does not evaporate easily. Even after removal with paper points, undiluted DMSO may remain pooled and the apical third acts as a strong solvent. As a result, the components of Theracal may be diluted, which can comprise the formation of polymer chains and bond strengths.

A different trend was observed for MTA, pretreatments had no effects on bond strengths, except for undiluted ethanol (EtOH). Lower bond strengths at the apical third were obtained after pretreating dentin with undiluted ethanol. Ethanol is highly miscible in water and replaces residual water molecules inside dentin tubules. This drastically reduces the intrinsic wetness of root canals [54]. Since MTA relies on proper hydration for adequate setting [55,56], ethanol dehydration resulted in lower bond strengths at the apical third. Higher dentinal tubule density at the coronal and middle thirds certainly contributed to lower dehydration levels due to the overall higher water content inside tubules. Higher moisture levels certainly prevented bond strength reductions. Differently, diluted ethanol had no negative effects on the bond strengths of MTA at the apical third due to the presence of water in the pretreatment solution. Since DMSO does not have the ability to dehydrate dentin, but rather acts by displacing water molecules, no negative effects were observed for MTA despite root segments.

Intraradicular bond strengths of S-PRG were not affected by any of the dentin pretreatments. None of the pretreatments were able to revert reductions in bond strength at the apical third. The bond strength of S-PRG at the apical third for treated and untreated were comparable. Further studies of the push-out bond strength at longer incubation times are needed to evaluate the long-term bonding ability of bioactive cements to root dentin.

6. Conclusion

Intraradicular bond strengths of the different bioactive cements varied depending on their composition and the root canal depth. Solvent-based pretreatments containing DMSO might improve intraradicular bonding of resin-modified bioactive cements in a concentration-dependent manner. However, different pretreatment methods should be applied with extreme caution, especially when combined with hydraulic bioactive cements.

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CRediT authorship contribution statement

Ikram Aqel Salim: Writing – original draft, Resources, Methodology, Investigation. **Anas Aaqel Salim:** Writing – original draft, Methodology, Investigation. **Thiago Henrique Scarabello Stape:** Writing – review & editing, Validation, Methodology, Formal analysis. **Mustafa Murat Mutluay:** Supervision, Formal analysis, Data curation. **Arzu Tezvergil-Mutluay:** Writing – review & editing, Supervision, Resources, Funding acquisition.

Declaration of competing interest

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

Data availability

Data will be made available on request.

References

[1] Torabinejad M, Pitt Ford TR. Root end filling materials: a review. Endod Dent Traumatol 1996;12:161–78. https://doi.org/10.1111/j.1600-9657.1996.tb00510.x.

[2] Ribeiro DA. Do endodontic compounds induce genetic damage? A comprehensive review. Oral Surg Oral Med Oral Pathol Oral Radiol Endod 2008;105:251–6. https://doi.org/10.1016/j.tripleo.2007.07.045.

[3] Amoroso-Silva PA, Marciano MA, Guimarães BM, Duarte MAH, Sanson AF, Moraes IG de. Apical adaptation, sealing ability and push-out bond strength of five root-end filling materials. Braz Oral Res 2014;28. https://doi.org/10.1590/1807-3107bor-2014.vol28.0043.

[4] Alhashimi RA, Mannocci F, Sauro S. Bioactivity, cytocompatibility and thermal properties of experimental Bioglass-reinforced composites as potential root-canal filling materials. J Mech Behav Biomed Mater 2017;69:355–61. https://doi.org/10.1016/j.jmbbm.2017.01.022.

[5] Abedi-Amin A, Luzi A, Giovarruscio M, Paolone G, Darvizeh A, Agulló VV, et al. Innovative root-end filling materials based on calcium-silicates and calcium-phosphates. J Mater Sci Mater Med 2017;28:1–10. https://doi.org/10.1007/S10856-017-5847-1/METRICS.

[6] Torabinejad M, Parirokh M. Mineral trioxide aggregate: a comprehensive literature review-Part II: leakage and biocompatibility investigations. 36, https://doi.org/10.1016/j.joen.2009.09.010; 2010.

[7] Girish Cs, Ponnappa K, Girish T, Ponappa M. Sealing ability of mineral trioxide aggregate, calcium phosphate and polymethylmethacrylate bone cements on root ends prepared using an Erbium: yttriumaluminium garnet laser and ultrasonics evaluated by confocal laser scanning microscopy. J Conserv Dent 2013;16:304. https://doi.org/10.4103/0972-0707.114355.

[8] Turk T, Fidlerb A. Effect of medicaments used in endodontic regeneration technique on push-out bond strength of MTA and Biodentine. Biotechnol Biotechnol Equip 2016;30:140–4. https://doi.org/10.1080/13102818.2015.1109477.

[9] Farrugia C, Baca P, Camilleri J, Arias Moliz MT. Antimicrobial activity of ProRoot MTA in contact with blood. Sci Rep 2017;7. https://doi.org/10.1038/srep41359.

[10] Gomes-Filho JE, Rodrigues G, Watanabe S, Estrada Bernabé PF, Lodi CS, Gomes AC, et al. Evaluation of the tissue reaction to fast endodontic cement (CER) and angelus MTA. J Endod 2009;35:1377–80. https://doi.org/10.1016/j.joen.2009.06.010.

[11] Porter ML, Bertó A, Primus CM, Watanabe I. Physical and chemical properties of new-generation endodontic materials. J Endod 2010;36:524–8. https://doi.org/10.1016/j.joen.2009.11.012.

[12] Torabinejad M, Hong CU, McDonald F, Pitt Ford TR, Pittford T. Physical and chemical properties of a new root-end filling material. J Endod 1995;21:349–53. https://doi.org/10.1016/S0099-2399(06)80967-2.

[13] Solanki N, Venkappa K, Shah N. Biocompatibility and sealing ability of mineral trioxide aggregate and biodentine as root-end filling material: a systematic review. J Conserv Dent 2018;21:10–5. https://doi.org/10.4103/JCD.JCD_45_17.

[14] Gandolfi MG, Siboni F, Prati C. Chemical-physical properties of TheraCal, a novel light-curable MTA-like material for pulp capping. Int Endod J 2012;45:571–9. https://doi.org/10.1111/j.1365-2591.2012.02013.x.

[15] Makkar S, Kaur H, Aggarwal A, Vashisht R. A confocal laser scanning microscopic study evaluating the sealing ability of mineral trioxide aggregate, biodentine and anew pulp capping agent-theracal. Dent J Adv Stud 2015;3:20–5. https://doi.org/10.1055/s-0038-1672009.

[16] Byoung S, Mark C, Rui Y, David EM. Polymerizable dental pulp healing, capping, and lining material and method for use. International patent A61K33/42; A61K33/42 application number WO2008US54387 20080220. Google Patents; 2008. ; Publication number WO2008103712 (A2).

[17] Ikemura K, Tay FR, Endo T, Pashley DH. A review of chemical-approach and ultramorphological studies on the development of fluoride-releasing dental adhesives comprising new pre-reacted glass ionomer (PRG) fillers. Dent Mater J 2008;27:315–39. https://doi.org/10.4012/dmj.27.315.

[18] Saku S, Kotake H, Scougall-Vilchis RJ, Ohashi S, Hotta M, Horiuchi S, et al. Antibacterial activity of composite resin with glass-ionomer filler particles. Dent Mater J 2010;29:193–8. https://doi.org/10.4012/dmj.2009-050.

[19] Shimazu K, Ogata K, Karibe H. Evaluation of the ion-releasing and recharging abilities of a resin-based fissure sealant containing S-PRG filler. Dent Mater J 2011;30:923–7. https://doi.org/10.4012/dmj.2011-124.

[20] Hosoya Y, Tadokoro K, Otani H, Hidaka K, Inoue T, Miyazaki M, et al. Effect of ammonium hexafluorosilicate application for arresting caries treatment on demineralized primary tooth enamel. J Oral Sci 2013;55:115–21. https://doi.org/10.2334/josnusd.55.115.

[21] Fujimoto Y, Iwasa M, Murayama R, Miyazaki M, Nagafuji A, Nakatsuka T. Detection of ions released from S-PRG fillers and their modulation effect. Dent Mater J 2010;29:392–7. https://doi.org/10.4012/dmj.2010-015.

[22] Ito S, Iijima M, Hashimoto M, Tsukamoto N, Mizoguchi I, Saito T. Effects of surface pre-reacted glass-ionomer fillers on mineral induction by phosphoprotein. J Dent 2011;39:72–9. https://doi.org/10.1016/j.jdent.2010.10.011.

[23] Iijima M, Ito S, Nakagaki S, Kohda N, Muguruma T, Saito T, et al. Effects of immersion in solution of an experimental toothpaste containing S-PRG filler on like-remineralizing ability of etched enamel. Dent Mater J 2014;33:430–6. https://doi.org/10.4012/dmj.2013-224.

[24] Stape THS, Seseogullari-Dirihan R, Tjäderhane L, Abuna G, Martins LRM, Tezvergil-Mutluay A. A novel dry-bonding approach to reduce collagen degradation and optimize resin-dentin interfaces. Sci Rep 2018;8:16890. https://doi.org/10.1038/s41598-018-34726-8.

[25] Stape THS, Tjäderhane L, Abuna G, Sinhoreti MAC, Martins LRM, Tezvergil-Mutluay A. Optimization of the etch-and-rinse technique: new perspectives to improve resin–dentin bonding and hybrid layer integrity by reducing residual water using dimethyl sulfoxide pretreatments. Dent Mater 2018;34:967–77. https://doi.org/10.1016/j.dental.2018.03.010.

[26] Salim Al-ani AA, Mutluay M, Stape THS, Tjäderhane L, Tezvergil- Mutluay A. Effect of various dimethyl sulfoxide concentrations on the durability of dentin bonding and hybrid layer quality. Dent Mater J 2018;37:501–5. https://doi.org/10.4012/dmj.2017-213.

[27] Stape THS, Tezvergil-Mutluay A, Mutluay MM, Martins LRM, do Prado RL, Pizi ECG, et al. Influence of dimethyl sulfoxide used as a solvent on the physical properties and long-term dentin bonding of hydrophilic resins. J Mech Behav Biomed Mater 2016;64:220–8. https://doi.org/10.1016/j.jmbbm.2016.07.003.

[28] Stape THS, Tjäderhane L, Tezvergil-Mutluay A, Yanikian CRF, Szesz AL, Loguercio AD, et al. Dentin bond optimization using the dimethyl sulfoxide-wet bonding strategy: a 2-year in vitro study. Dent Mater 2016;32:1472–81. https://doi.org/10.1016/j.dental.2016.09.015.

[29] Stape THS, Tjäderhane L, Marques MR, Aguiar FHB, Martins LRM. Effect of dimethyl sulfoxide wet-bonding technique on hybrid layer quality and dentin bond strength. Dent Mater 2015;31:676–83. https://doi.org/10.1016/j.dental.2015.03.008.

[30] Carvalho CA, Cantoro A, Mazzoni A, Goracci C, Breschi L, Ferrari M. Effect of ethanol application on post-luting to intraradicular dentine. Int Endod J 2009;42:129–35. https://doi.org/10.1111/j.1365-2591.2008.01491.x.

[31] Ismail OA, Stape THS, Tezvergil-Mutluay A. Concentration effect of DMSO-dry bonding on the stability of etch-and-rinse bonds. Dent Mater 2023;39:1113–21. https://doi.org/10.1016/j.dental.2023.09.013.

[32] Tjäderhane L, Mehtälä P, Scaffa P, Vidal C, Pääkkönen V, Breschi L, et al. The effect of dimethyl sulfoxide (DMSO) on dentin bonding and nanoleakage of etch-and-rinse adhesives. Dent Mater 2013;29:1055–62. https://doi.org/10.1016/j.dental.2013.07.014.

[33] Mjör IA. Dentin permeability: the basis for understanding pulp reactions and adhesive technology. Braz Dent J 2009;20:3–16. https://doi.org/10.1590/S0103-64402009000100001.

[34] Stape THS, Uctasli M, Cibelik HS, Tjäderhane L, Tezvergil-Mutluay A. Dry bonding to dentin: broadening the moisture spectrum and increasing wettability of etch-and-rinse adhesives. Dent Mater 2021;37:1676–87. https://doi.org/10.1016/j.dental.2021.08.021.

[35] El-Ma'Aita AM, Qualtrough AJE, Watts DC. The effect of smear layer on the push-out bond strength of root canal calcium silicate cements. Dent Mater 2013;29:797–803.

[36] Yassen GH, Huang R, Al-Zain A, Yoshida T, Gregory RL, Platt JA. Evaluation of selected properties of a new root repair cement containing surface pre-reacted glass ionomer fillers. Clin Oral Invest 2016;20:2139–48. https://doi.org/10.1007/s00784-016-1715-5.

[37] Skidmore LJ, Berzins DW, Bahcall JK. An in vitro comparison of the intraradicular dentin bond strength of resilon and gutta-percha. J Endod 2006;32:963–6. https://doi.org/10.1016/j.joen.2006.03.020.

[38] Goracci C, Tavares AUFA, et al. The adhesion between fibre posts and root canal walls: comparison between microtensile and push-out bond strength measurements. Eur J Oral Sci 2004;112:353–61.

[39] Collares FM, Portella FF, Rodrigues SB, Celeste RK, Leitune VCB, Samuel SMW. The influence of methodological variables on the push-out resistance to dislodgement of root filling materials: a meta-regression analysis. Int Endod J 2015;49:836–49. https://doi.org/10.1111/iej.12539.

[40] Gasperi TL, da Silveira J de AC, Schmidt TF, Teixeira C da S, Garcia L, da FR, et al. Physical-mechanical properties of a resin-modified calcium silicate material for pulp capping. Braz Dent J 2020;31:252–6. https://doi.org/10.1590/0103-6440202003079.

[41] Reyes-Carmona JF, Felippe MS, Felippe WT. The biomineralization ability of mineral trioxide aggregate and portland cement on dentin enhances the push-out strength. J Endod 2010;36:286–91. https://doi.org/10.1016/j.joen.2009.10.009.

[42] Iacono F, Gandolfi MG, Huffman B, Sword J, Agee K, Siboni F, et al. Push-out strength of modified Portland cements and resins. Am J Dent 2010;23:43–6.

[43] Radulica N, Sanz JL, Lozano A. Dentin bond strength of calcium silicate-based materials: a systematic review of in vitro studies. Appl Sci 2024;14. https://doi.org/10.3390/app14010104.

[44] Han L, Okiji T. Evaluation of the ions release/incorporation of the prototype S-PRG filler-containing endodontic sealer. Dent Mater J 2011;30:898–903. https://doi.org/10.4012/dmj.2011-101.

[45] Bennett AW, Watts DC. Performance of two blue light-emitting-diode dental light curing units with distance and irradiation-time. Dent Mater 2004;20:72–9. https://doi.org/10.1016/S0109-5641(03)00070-8.

[46] Ferrari M, Mannocci F, Vichi A, Cagidiaco MC, Mjör IA. Bonding to root canal: structural characteristics of the substrate. Am J Dent 2000;13:255–60.

[47] Mannocci F, Pilecki P, Bertelli E, Watson TF. Density of dentinal tubules affects the tensile strength of root dentin. Dent Mater 2004;20:293–6. https://doi.org/10.1016/S0109-5641(03)00106-4.

[48] Paqué F, Luder HU, Sener B, Zehnder M. Tubular sclerosis rather than the smear layer impedes dye penetration into the dentine of endodontically instrumented root canals. Int Endod J 2006;39:18–25. https://doi.org/10.1111/j.1365-2591.2005.01042.x.

[49] Reyes-Carmona JF, Felippe MS, Felippe WT. Biomineralization ability and interaction of mineral trioxide aggregate and white portland cement with dentin in a phosphate-containing fluid. J Endod 2009;35:731–6. https://doi.org/10.1016/j.joen.2009.02.011.

[50] Ulusoy Paltun YN, Güven N, Çelik B. Dislodgement resistance of calcium silicate-based materials from root canals with varying thickness of dentine. Int Endod J 2016;49:1188–93. https://doi.org/10.1111/iej.12573.

[51] Darvell BW, Wu RCT. MTA - an hydraulic silicate cement: review update and setting reaction. Dent Mater 2011;27:407–22. https://doi.org/10.1016/j.dental.2011.02.001.

[52] Stape THS, Mutluay MM, Tjäderhane L, Uurasjärvi E, Koistinen A, Tezvergil-Mutluay A. The pursuit of resin-dentin bond durability: simultaneous enhancement of collagen structure and polymer network formation in hybrid layers. Dent Mater 2021;37:1083–95. https://doi.org/10.1016/j.dental.2021.03.010.

[53] Gupta SN, Nandi US. Role of dimethyl sulfoxide as a solvent for vinyl polymerization. J Polym Sci 1 Polym Chem 1970;8:1493–501. https://doi.org/10.1002/pol.1970.150080614.

[54] Liu Y, Tjäderhane L, Breschi L, Mazzoni A, Li N, Mao J, et al. Limitations in bonding to dentin and experimental strategies to prevent bond degradation. J Dent Res 2011;90:953–68. https://doi.org/10.1177/0022034510391799.

[55] Camilleri J. Mineral trioxide aggregate: present and future developments. Endod Top 2015;32:31–46. https://doi.org/10.1111/etp.12073.

[56] Dawood AE, Parashos P, Wong RHK, Reynolds EC, Manton DJ. Calcium silicate-based cements: composition, properties, and clinical applications. J Investig Clin Dent 2017;8:e12195. https://doi.org/10.1111/jicd.12195.