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Using Proanthocyanidin as a Root Dentin Conditioner for GIC Restorations

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Abstract

Glass ionomer cements (GICs) are considered the material of choice for restoration of root carious lesions (RCLs). When bonding to demineralized dentin, the collapse of dentinal collagen during restorative treatment may pose challenges. Considering its acidic nature and collagen biomodification effects, proanthocyanidin (PAC) could be potentially used as a dentin conditioner to remove the smear layer while simultaneously acting to biomodify the dentinal collagen involved in the bonding interface. In this study, 6.5% w/v PAC was used as a conditioner for sound (SD) and laboratory demineralized (DD) root dentin before bonding to resin-modified GIC (FII), casein phosphopeptide–amorphous calcium phosphate (CPP-ACP)–modified GIC (FVII), or a high-viscosity GIC (FIX). Root dentin conditioned with deionized distilled water (DDW) or polyacrylic acid (PAA) served as controls. Results indicated FII showed higher shear bond strength (SBS) on SD than the other 2 GICs, especially in PAA-conditioned samples; FIX showed significantly higher SBS than FII and FVII on PAA- or PAC-conditioned DD. In each category of GIC, PAA and PAC did not have a significant influence on SBS in most cases compared to DDW except for a significant decrease in PAC-conditioned SD bonded to FII and a significant increase in PAA-conditioned DD bonded to FIX. The bonding interface between GIC and SD was generally more resistant to the acid-base challenge than DD. Although the alterations in failure modes indicated a compromised interfacial interaction between GICs and PAC-treated root dentin, biomodification effects of PAC on dentin were observed from Raman microspectroscopy analysis in terms of the changes in mineral-to-matrix ratio and hydroxyproline-to-proline ratio of dentin adjacent to the bonding interface, especially of DD. Results from this study also indicated the possibility of using in situ characterization such as Raman microspectroscopy as a complementary approach to SBS test to investigate the integrity of the bonding interface.

Keywords: root caries, glass ionomer cements, collagen crosslinking, dentin bonding, biomodification, grape seed extract

Introduction

Demographic transitions and improved oral health care have contributed to increased tooth retention in the elderly. Consequently, the prevalence of root caries is increasing due to age-associated gingival recession exposing caries-prone root surfaces to the oral environment and supragingival biofilm (Heasman et al. 2017). Restorative treatment of root caries can be particularly challenging due to the structure and composition of root dentin and lesion shape giving rise to complex restorative procedures and clinical conditions.

Dentin is a hierarchically structured biocomposite composed of an organic matrix impregnated with matrix-mediated carbonated hydroxyapatite (Veis 2005). Restorative materials applied to dentin can penetrate into and form complex nanostructural interactions with the dentinal organic matrix (Bertassoni et al. 2012). In particular, restorative materials are placed frequently on partially demineralized hard tissues according to the tenet of minimally invasive carious tissue removal advocating preservation of demineralized but remineralizable dentin (not at the margins) (Schwendicke et al. 2016). The exposed demineralized dentinal collagen might impose difficulties in infiltration of restorative materials into dentin matrices when a hybrid layer is involved in bonding, possibly leaving the formed interface more susceptible to degradation (Tjäderhane et al. 2013). Nevertheless, the remineralizable dentin remains structurally intact with the dentinal collagen undergoing reversible alterations in intermolecular crosslinks (Kuboki et al. 1977; Schwendicke et al. 2016). Therefore, application of exogenous crosslinking agents to reinforce dentinal collagen seems promising, contributing to a

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more stable bonding interface. Recently, biocompatible naturally derived crosslinking agents such as proanthocyanidin (PAC) have gained increasing interest for their ability to biomodify dentinal collagen and improve the mechanical properties and enzymatic resistance of dentin matrices, thus forming a more stable interface between dentin and restorative materials (Leme-Kraus et al. 2017; Shavandi et al. 2018).

Despite advances in restorative materials, restoring root carious lesions (RCLs) can still be problematic due to the difficulties in moisture control and isolation of bonding areas from oral fluids (Momoi et al. 2016; Heasman et al. 2017). In addition, hyposalivation due to aging and medications in older adults could further increase the susceptibility for caries lesion development around restorations and on other root surfaces (Gueiros et al. 2009). Therefore, glass ionomer cements (GICs), with a tolerance to moisture, chemical adhesion to tooth structure, and anticariogenic properties, might be the material of choice for RCL restorations (Watson et al. 2014). In particular, the introduction of high-viscosity GIC and resin-modified GIC ensures high mechanical strength and wear resistance of GIC materials along with the casein phosphopeptide–amorphous calcium phosphate (CPP-ACP; Recaldent)–modified GIC showing enhanced ion-releasing abilities for caries prevention (Sidhu and Nicholson 2016; Shen et al. 2020). Adhesion of GICs to dentin depends predominantly on chemical bonding resulting from continuous ion exchange and micromechanical interlocking arising from the cement tags within dentinal tubules or hybridizing with mineral-coated dentinal collagen (Zoergiebel and Ilie 2013). However, dental instrumentation prior to bonding results in a 1- to 2-µm-thick smear layer composed of debris, including denatured collagen attached to the underlying dentin surface. Bonding to this irregular contaminant results in a weak link at the dentin-GIC interface (Pashley 1992). Therefore, dentin surface conditioners, for example, polyacrylic acid (PAA) and tannic acid, have been used before bonding to remove the smear layer by interacting with dentin via a multiplicity of functional groups. However, high concentrations or long application times of conditioners can lead to partially demineralized subsurface zones and exposed dentinal collagen beneath the intermediate layer between dentin and GICs (Powis et al. 1982). As a condensed tannin, PAC is acidic in nature and able to demineralize dentin surfaces (Cai et al. 2019). Along with its crosslinking effects, PAC could potentially be used as a dentin conditioner to remove the smear layer while simultaneously acting to biomodify the exposed dentinal collagen involved in the bonding interface.

Therefore, the aim of this study was to investigate the effects of PAC used as a dentin conditioner on the adhesion and interfacial interactions of 3 GICs, that is, high-viscosity GIC, resin-modified GIC, and CPP-ACP–modified GIC to sound and laboratory demineralized root dentin. Root dentin conditioned with deionized distilled water or PAA served as controls.

Materials and Methods

Root Dentin Preparation

Root dentin specimens (n = 195) were prepared from the midregion of noncarious dental roots and wet polished with 600-grit SiC paper to expose flat root dentin surfaces and create a standard smear layer. Specimens were divided into 2 main groups: sound dentin (SD) and demineralized dentin (DD), where the latter was created using acetate-based demineralizing solution containing 50 mM acetic acid, 2.2 mM $CaCl_2$, and 2.2 mM KH_2PO_4 with pH adjusted to 5 with KOH. Both SD and DD were divided into 3 subgroups, conditioned with deionized distilled water (DDW), Cavity Conditioner (20% PAA; GC Corp), or 6.5 w/v% PAC solution (International Laboratory; containing >95% oligomeric PAC), respectively.

Shear Bond Strength Testing

Three types of GICs—that is, light-cured resin-modified GIC (FII) (Fuji II LC; GC Corp.), 3% CPP-ACP–modified GIC (FVII) (Fuji VII EP; GC Corp.), and high-viscosity GIC (FIX) (Fuji IX GP EXTRA; GC Corp.)—were applied to the conditioned-dentin surfaces using a cylindrical mold (SDI Limited) of 5 mm height and 3.5 mm diameter. Each specimen was stored separately in 100% relative humidity (RH) at 37°C for 24 h (Fig. 1). The shear bond strength (SBS) testing (n = 15 per group) was performed using a universal testing machine (Instron 5544; Instron), where SBS values were calculated as the function of stress distribution.

Failure Mode Analysis

The debonded specimens from SBS testing were observed under a light microscope (DM2000; Leica Microsystems), where failures were classified into interfacial, cohesive, mixed, or pretest failures and expressed as percentages.

Morphology of Conditioned-Dentin Surfaces

Conditioned-dentin surfaces (n = 2 per group) were dehydrated using ascending concentrations of ethanol, sputter-coated, and imaged using scanning electron microscopy (SEM) (ESEM Quanta 200; FEI Company).

Acid-Base Technique

The GIC-dentin bonding interfaces (n = 2 per group) were observed using SEM after treatment with an acid-base technique, where the bonding interface was treated with 10% orthophosphoric acid for 10 s and then 5% sodium hypochlorite for 5 min to remove the inorganic and organic components of dentin, respectively.

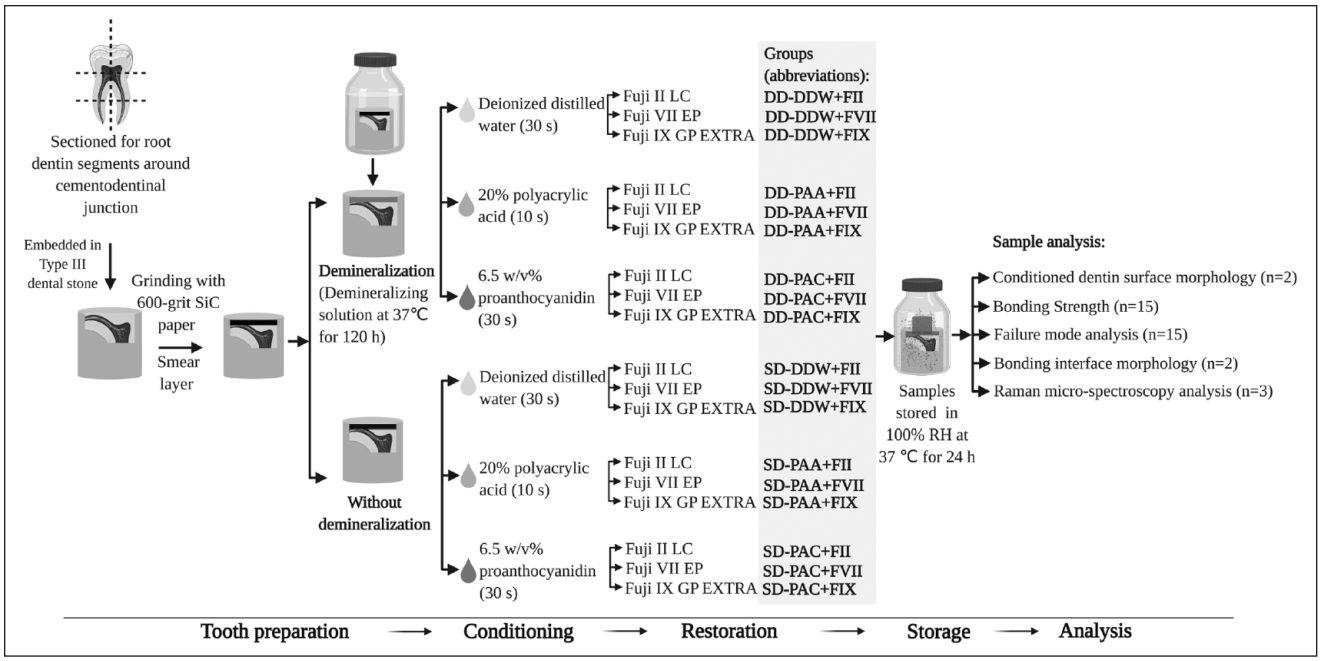

Figure 1. Schematic diagram of experimental design and groups (abbreviations) in this study.

Raman Microspectroscopy

Chemical properties of dentin around bonding interfaces were characterized using confocal Raman microspectroscopy (Renishaw inVia Qontor) with a 785-nm diode. The crystallinity of dentin minerals ($HAP_{crystallinity}$), mineral-to-matrix (amide I) ratio (MMR), and hydroxyproline-to-proline ratio were determined from the Raman spectra ($n = 3$ per group).

Statistical Analysis

Statistical analysis was conducted by using SPSS 22.0 software (SPSS, Inc.). The normal distribution and equality of variances of data were confirmed by the Shapiro-Wilk test and Levene's test, respectively. Three-way analyses of variance (ANOVAs) with specific contrasts were performed for the analysis of SBS and parameters from Raman microspectroscopy of the bonded specimens with 3 variables: GIC (FII, FVII, or FIX), dentin substrate (SD or DD), and conditioner (DDW, PAA, or PAC). Two-way ANOVA were performed for the analysis of parameters from Raman microspectroscopy of dentin surfaces with 2 variables: dentin substrate (SD or DD) and conditioner (DDW, PAA, or PAC). Failure modes were analyzed using the χ^2 test. Statistical significance was set at $\alpha = 0.05$.

Further details of materials and methods are available in the Appendix.

Results

Shear Bond Strength

Three-way ANOVA indicated 4 significant interactions: GIC × conditioner, GIC × dentin substrate, conditioner × dentin substrate, and GIC × conditioner × dentin substrate ($P < 0.05$), in SBS values (Appendix Table 3).

PAA and PAC conditioning did not have a significant influence on SBS of GICs in most cases except for a significant decrease in PAC-conditioned SD bonded to FII and a significant increase in PAA-conditioned DD bonded to FIX. Compared to PAA conditioning, PAC resulted in significantly decreased SBS of all 3 GICs bonded to DD (Fig. 2A).

When different categories of GICs were compared, FII showed higher SBS on DDW-conditioned SD than the other 2 GICs. This advantage was more pronounced with PAA conditioning. FIX showed significantly higher SBS than FII and FVII on DD conditioned with PAA or PAC (Fig. 2A).

Failure Modes

Different conditioning protocols affected the distribution of failure modes of GICs significantly (Appendix Table 2). Specifically, the proportion of cohesive failures within GICs increased when bonded to PAA-conditioned SD. However, after PAC conditioning, failures were predominantly mixed and interfacial modes with a few occurring before testing. In addition, a higher proportion of cohesive failures was observed in FVII than the other 2 GICs.

When bonded to DD, the mixed failure mode was dominant. PAA conditioning significantly increased the proportion of cohesive failures in FVII and FIX, while PAC conditioning increased pretest failures in FII, and FVII and contributed to more interfacial failures in FVII and FIX (Fig. 2B; Appendix Table 2).

Morphology of Conditioned-Dentin Surfaces and Bonding Interface

PAA or PAC conditioning of SD or DD partially removed the smear layer and exposed the dentinal tubules to different extents (Fig. 3A–F).

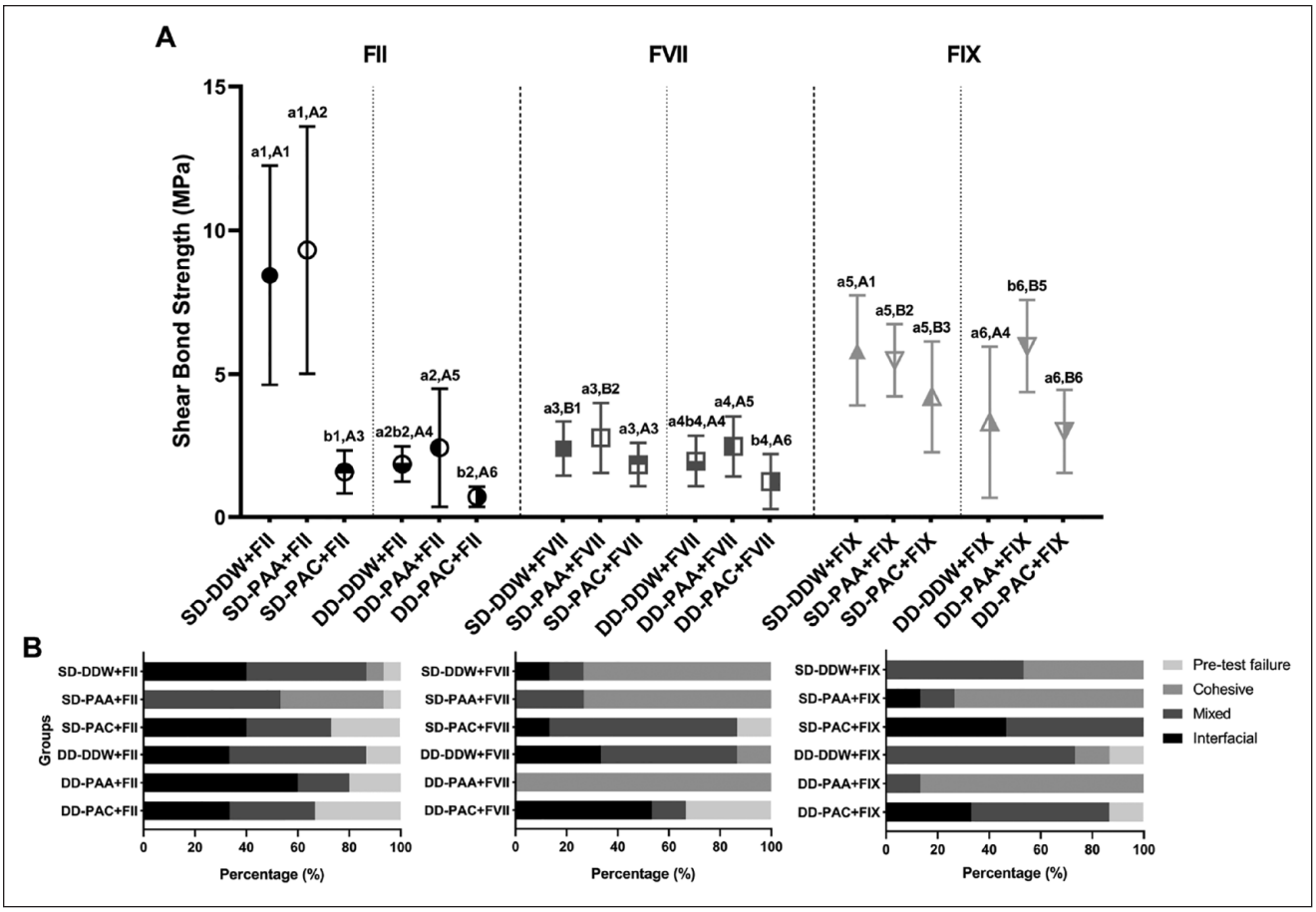

Figure 2. Shear bond strength (SBS) test of root dentin bonded to different glass ionomer cements (GICs) and failure mode analysis. (**A**) SBS values (MPa; mean ± standard deviation) grouped by the category of GICs (FII, FVII, or FIX) and (**B**) failure modes (percentage) of FII, FVII, and FIX bonded to sound dentin (SD) or demineralized dentin (DD) conditioned with distilled deionized water (DDW), polyacrylic acid (PAA), or proanthocyanidin (PAC) after 24 h storage in 100% relative humidity ($n = 15$ per group). Different lowercase and uppercase letters above each column in (A) indicate statistically significant differences ($P < 0.05$) in SBS within SD or DD treated with different conditioners and bonded to the same GIC and within the same dentin substrates bonded to different GICs, respectively (3-way analysis of variance with specific contrasts).

An acid-base resistant (ABR) layer appeared at the interface between SD and GICs, being most pronounced between FIX and SD conditioned with either PAA or PAC, where long, thick funnel-shaped tags of cement were observed (Fig. 3c2). ABR layers with resin tags and intimate adaptation were observed between FII and DD; in particular, PAA-treated DD showed a thick cement infiltration zone into the dentin matrix (Fig. 3a5).

Raman Microspectroscopy

Demineralization led to substantial decreases in the intensity of $\nu_1(PO_4^{3-})$ (959–960 cm^{-1}) and B-type carbonate (1,070 cm^{-1}) of hydroxyapatite (Fig. 4A–D). The peaks located at approximately 1,263 cm^{-1} and 1,455 cm^{-1} in PAC-DD samples represented the PAA salts from GICs (Young et al. 2000; Atmeh et al. 2012) (Fig. 4A–C).

Demineralization and conditioners did not influence the $HAP_{crystallinity}$ of dentin surfaces ($P > 0.05$) (Fig. 5A1). Three-way ANOVA of $HAP_{crystallinity}$ indicated no significant interactions between the 3 variables: GIC, dentin substrate, and conditioner ($P > 0.05$) (Appendix Table 4). FVII restoration on PAA-conditioned DD led to increased $HAP_{crystallinity}$ (lower FWHM) of dentin adjacent to the bonding interface compared to the original SD (Fig. 5C1). No significant changes in the $HAP_{crystallinity}$ of dentin were observed after FII or FIX restoration (Fig. 5B1, D1).

Demineralization led to significantly decreased MMR of dentin surfaces. While conditioners did not influence the MMR of SD surfaces, PAC conditioning decreased MMR of DD surfaces significantly (Fig. 5A2). PAC-conditioned SD showed significantly lower MMR compared to PAA-conditioned SD when bonded to FVII or FIX. GIC restorations generally could not recover the MMR of DD (Fig. 5B2–D2) except for FII bonded to PAA-conditioned DD, which showed similar MMR to the original SD (Fig. 5B2).

In addition, demineralization led to a significant decrease of the hydroxyproline-to-proline ratio for dentin surfaces. While

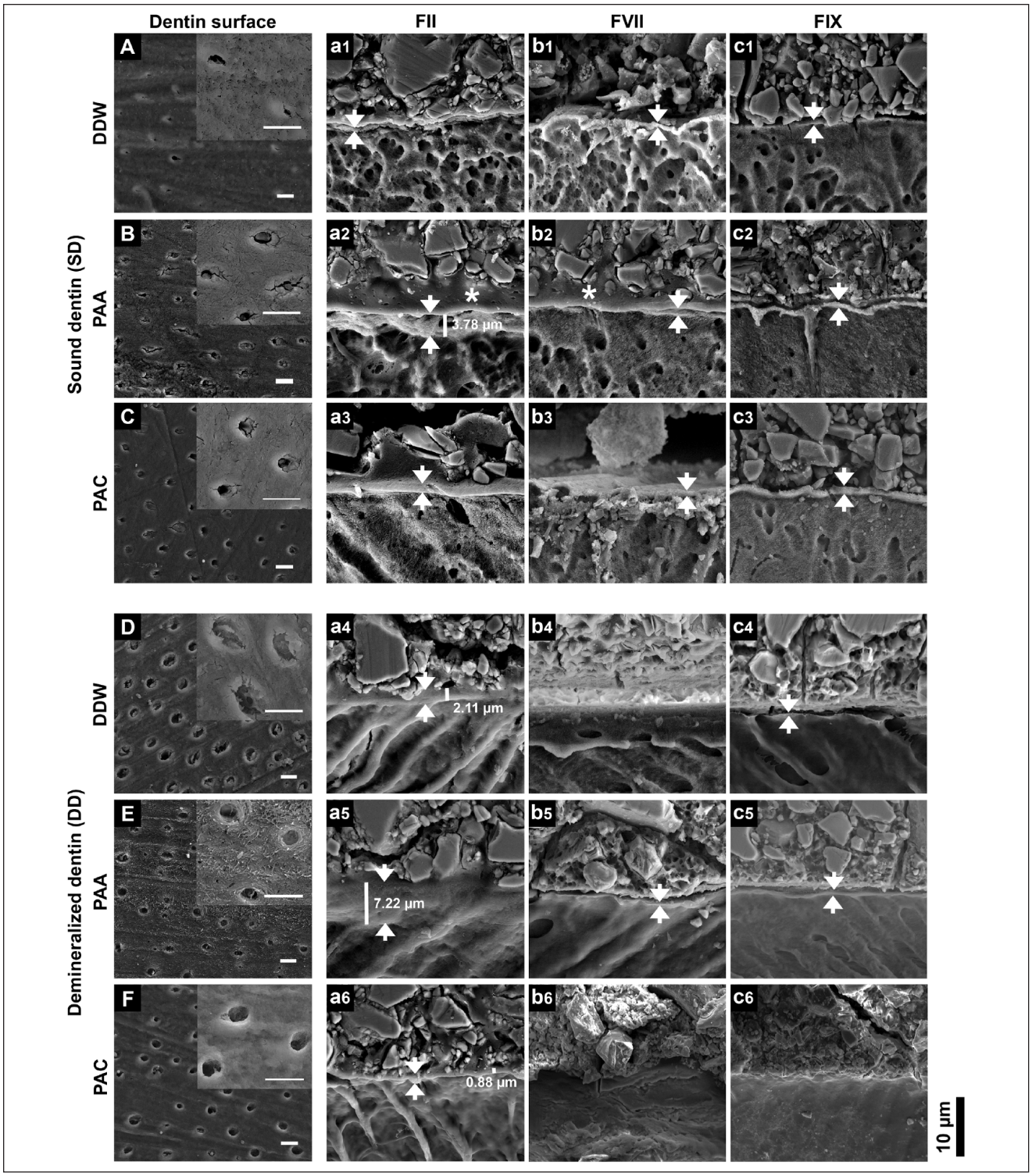

Figure 3. Scanning electron microscopy images of the conditioned root dentin surfaces and bonding interfaces. (**A–F**) Sound (SD) and demineralized (DD) root dentin surfaces with a standard smear layer conditioned with distilled deionized water (DDW), polyacrylic acid (PAA), or proanthocyanidin (PAC) (bar = 5 μm) and (a1–6, b1–6, c1–6) bonding interface between FII, FVII, or FIX and SD or DD conditioned with DDW, PAA, or PAC after the acid-base technique treatment. Arrows denote acid-base resistant (ABR) layers between glass ionomer cements (GICs) and dentin; asterisks (*) denote the absorption layer in GICs.

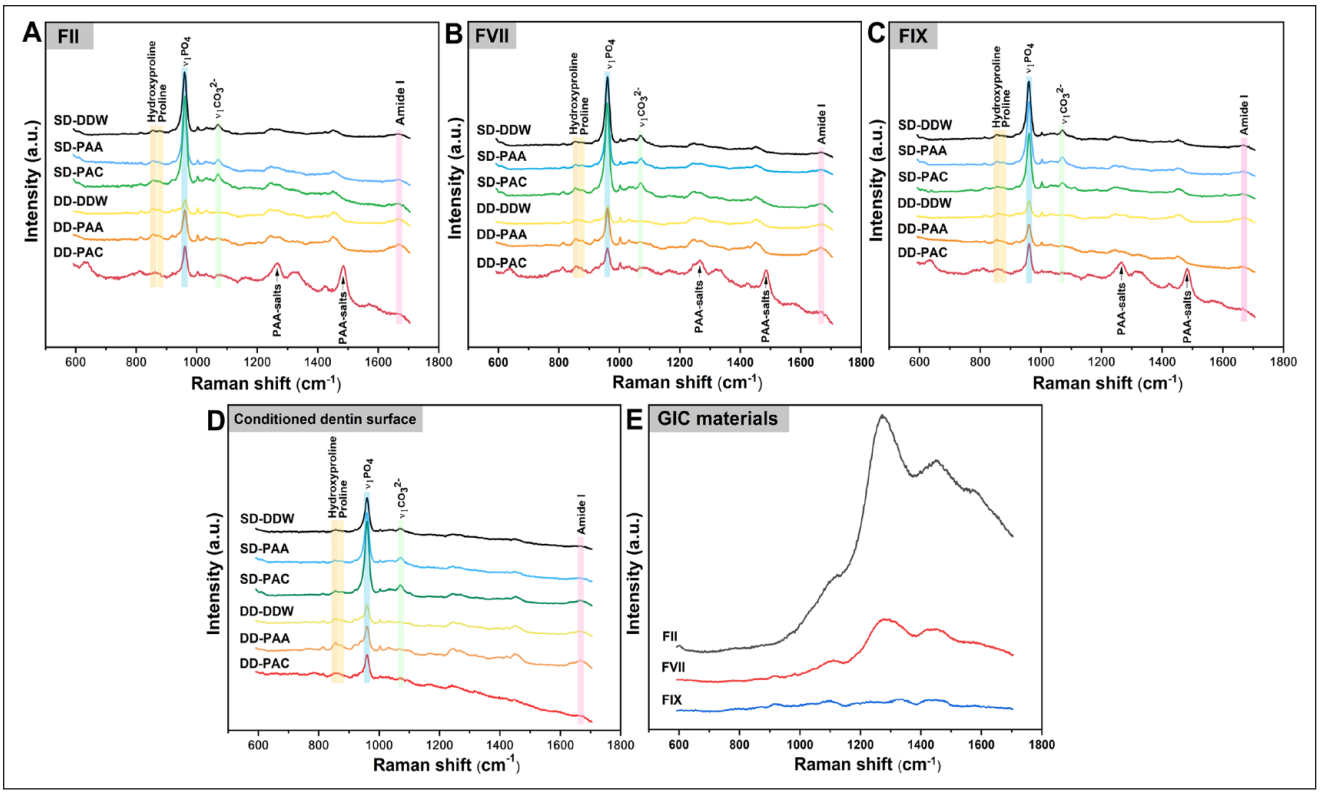

Figure 4. Raman spectra of root dentin adjacent to the bonding interface and glass ionomer cement (GIC) materials. (**A–C**) Cross-sectional surfaces of sound (SD) and demineralized (DD) root dentin adjacent to FII, FVII, or FIX in the bonding interface; (**D**) SD and DD surfaces conditioned with distilled deionized water (DDW), polyacrylic acid (PAA), or proanthocyanidin (PAC); and (**E**) FII, FVII, and FIX GIC materials.

conditioners did not influence the hydroxyproline-to-proline ratio of SD surfaces, this ratio for DD surfaces increased significantly after PAC conditioning (Fig. 5A3). This increase was also observed after placement of GICs (Fig. 5B3–D3). Moreover, this ratio of SD adjacent to the bonding interface with FIX also increased significantly with PAC conditioning (Fig. 5D3).

Discussion

In this study, an artificial RCL model was created using a demineralizing solution to simulate the clinically remineralizable dentin of RCLs. Although this model may not truly reflect a carious lesion, it has high reproducibility under controlled conditions with a similar degree of demineralization.

GICs with different formulations showed distinct bonding performance on root dentin in the short term. Specifically, when bonded to SD, the dual bonding mechanisms of FII resulted in higher SBS than the other 2 GICs, which rely on chemical reactions between PAA and hydroxyapatite, especially when SD was conditioned with PAA (Coutinho et al. 2007). FVII showed the lowest SBS compared to the other 2 GICs when bonded to DDW or PAA-conditioned SD. However, FVII debonded from dentin predominantly as cohesive failures within the material itself, possibly due to the incorporation of CPP-ACP that changes the powder composition and the inherent mechanical strength of GIC materials (Al Zraikat et al. 2011). The presence of CPP-ACP might also act as stress-concentration points initiating fracture within the material (Mazzaoui et al. 2003).

Restorative materials typically show decreased bond strength to carious dentin due to reduced minerals and increased water content in dentin and the formation of weak hybrid-like layers with the involvement of altered organic components (Saad et al. 2017). The present study confirmed the significantly different bond strength of GICs to DD and illustrated lower MMR of DD adjacent to the bonding interface compared to SD. With regard to the bonding performance of different GICs on DD, FIX showed significantly higher SBS than FII with PAA conditioning and comparable SBS to FII without conditioning. This result was not consistent with previous studies where traditional GIC showed lower bond strength than resin-modified GIC when bonded to caries-affected dentin (Palma-Dibb et al. 2003; Choi et al. 2006). This distinction could be related to the degree of demineralization and organic/inorganic components of DD substrates where GICs were bonded (Marshall et al. 1997). Particularly, demineralized root dentin with low mineral content along with a denatured collagen fibril network was not suitable for chemical bonding and resin monomer penetration (Takahashi et al. 2013). In addition,

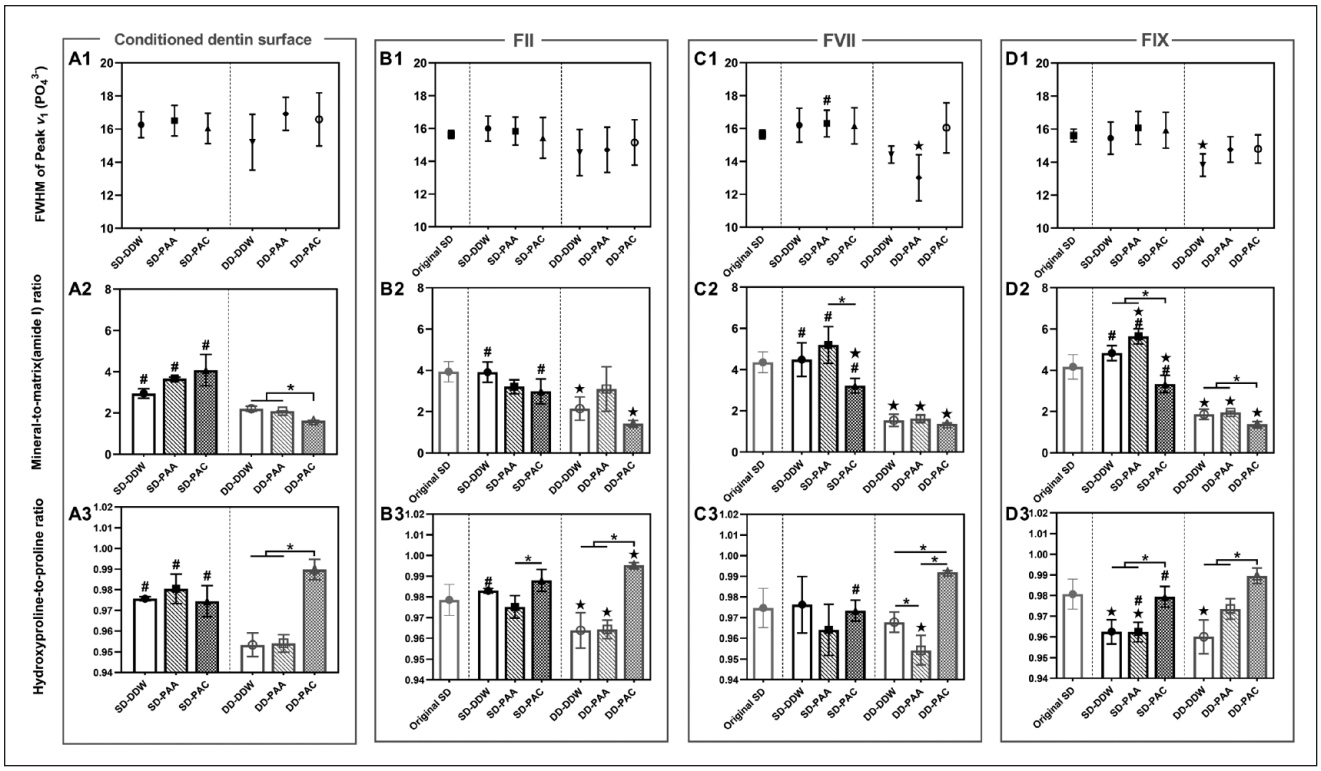

Figure 5. Parameters of root dentin adjacent to the bonding interface obtained from Raman spectra. (**A1–D1**) Full width at half maximum (FWHM) of peak $\nu_1(PO_4^{3-})$, (**A2–D2**) mineral-to-matrix (amide I) ratio (MMR), and (**A3–D3**) hydroxyproline-to-proline ratio of the conditioned dentin surface and the original sound dentin (SD), as well as SD and demineralized (DD) root dentin adjacent to FII, FVII, or FIX in the bonding interface according to Raman spectra ($n = 3$ per group). Asterisks (*) indicate significant differences ($P < 0.05$) between the groups connected by a line (i.e., significant differences [$P < 0.05$] from different glass ionomer cements [FII, FVII, or FIX]). Hashes (#) indicate significant differences ($P < 0.05$) from different dentin substrates (SD or DD) (3-way analysis of variance with specific contrasts). Stars (★) indicate significant differences ($P < 0.05$) between the indicated group and the original SD (Student's *t* test).

the presence of residual water in DD may change the powder/liquid ratio of GIC and dilute the concentration of 2-hydroxyethyl methacrylate (HEMA) in FII, thus reducing bonding efficacy. While FVII generally showed lower SBS on SD than FII and FIX, it demonstrated comparable bonding capacity on DD. Moreover, FVII bonded to PAA-conditioned DD resulted in increased crystallinity of the DD adjacent to the bonding interface compared to the original SD, indicating improved remineralization potential. Therefore, FVII, with enhanced release of Ca^{2+}, PO_4^{3-}, and F^-, is promising for minimally invasive RCL treatments, although limited data regarding the performance of FVII on root dentin are available (Mazzaoui et al. 2003).

The ion-exchange interface formed between GICs and SD was more resistant to the acid-base challenge compared to that formed with DD, similar to the situations when GICs were bonded to natural caries-affected dentin (Tanumiharja et al. 2000; Koizumi et al. 2016). Although the morphology and thickness of ABR layers is an indication of the quality of dentin-GIC interaction, no consistent correlation between bond strength and thickness of ABR layers could be concluded. Specifically, despite lower SBS of FII bonded to DD than to SD, the ABR layer in DD was well structured with resin tags, presumably because DD surfaces, with less smear layer and exposed dentinal tubules, have higher permeability to polyelectrolytes formed with PAA or resin monomers from FII. However, despite the enhanced penetration, incomplete infiltration of polyelectrolytes of high molecular weight into the interfibrillar spaces within dentinal collagen might result in weak links between FII and DD (Yip et al. 2001). This was similar to resin-based materials bonding to carious dentin where thick hybrid layers were observed despite reduced bond strength due to low tensile strength of carious tissues (Perdigão 2010).

PAA and PAC acted as mild and ultra-mild conditioners on root dentin, respectively, partially removing the smear layer without disturbing the smear plugs or overly widening the dentinal tubules in SD. When applied on DD, PAA (pH ~1.9) conditioning further demineralized intertubular dentin and exposed the collagen fibrils, while PAC (pH ~4.46) smoothed the morphology of dentin surfaces without significant alterations. The smoothed dentin surface topography after PAC conditioning could be ascribed to either smearing or formation of a layer of reaction products between dentinal collagen and PAC, similar to tannic acid conditioning (Powis et al. 1982). In addition, the functional groups in PAC and PAA (i.e., phenolic hydroxyls and carboxylic acid hydroxyls, respectively) putatively form a multiplicity of hydrogen bonds with dentin surfaces and potentially promote wetting, cleaning, and sorption of the conditioning agent onto dentin (Powis et al. 1982).

PAA conditioning altered the predominant failure mode between GICs and dentin toward cohesive debonding,

indicating a stronger bond strength that surpassed the shear strength of GICs. Although no significant difference in bond strength between GICs and SD was observed after PAA conditioning, consistent with a recent study (Hoshika et al. 2021), improved SBS was observed between GICs (especially FIX) and DD. In addition, PAA-conditioned DD showed comparable MMR to the original SD after bonded to FII due to increased mineral content after restoration. This promoting effect of PAA has also been observed for resin-modified GIC previously, attributed to the removal of smear layer and partial demineralization of underlying dentin, increasing the surface area and micro-porosities (Saad et al. 2017). Therefore, results from the present study agree with PAA conditioning prior to GIC bonding, especially when DD remains after carious tissue removal.

However, PAC conditioning used in the present study did not improve the bond strength of GICs to either SD or DD. GIC-dentin interaction relies on the wetting of dentin surfaces aided by the hydrophilic nature of conditioners; however, the bound water in dentin displaced by PAC-mediated collagen crosslinking altered the water dynamics of dentinal tissues, not favored by dentin-GIC contact (Powis et al. 1982; Fathima et al. 2010). Moreover, PAC has been reported to have insignificant crosslinking effects on the dentinal collagen protected by the mineral phase. Therefore, the crosslinking effect of PAC on SD bonded to GICs could be limited (Bedran-Russo et al. 2007). In addition, a previous clinical trial on resin-dentin bonding using PAC as a primer indicated the influence of PAC on resin free–radical polymerization (de Souza et al. 2020). This could also explain the decreased bond strength between FII and PAC-conditioned dentin. Nonetheless, PAC was reported to have high affinity for proline-rich protein (Hagerman and Butler 1981). As illustrated in the present study, PAC conditioning changed MMR of DD surfaces significantly presumably due to alterations in the Amide I band and increased the hydroxyproline-to-proline ratio of DD adjacent to the bonding interface. These 2 parameters indicated the changes of collagen secondary structures after crosslinking and possibly more additional sites for hydroxyapatite crystal nucleation on hydroxylated surfaces (Buckley et al. 2012).

Results from the present study indicated the adhesion and interfacial interaction between root dentin and GICs were dependent on the properties of GICs, dentin substrates, and the conditioners used. Although PAC used as a dentin conditioner for GIC bonding on root dentin did not improve the SBS of restorations, biomodification effects of PAC were observed in terms of the morphology and chemical properties (e.g., MMR, hydroxyproline-to-proline ratio) of the dentin adjacent to the bonding interface, especially for DD. Modification of PAC conditioning protocols in future studies is warranted to further clarify the effects of PAC conditioning on GIC bonding with root dentin. In addition, the present results demonstrate the limitation of SBS tests in evaluating the interaction between dentin and restorative materials. Specifically, the recorded bonding strength refers to the maximum strength at sudden crack propagation; therefore, it could not reveal the overall material-dentin interfacial integrity. In situ characterization of the material-dentin interface such as the Raman microspectroscopy used in the present study could be applied as a complementary approach to assess the properties and integrity of the bonding interface.

Author Contributions

J. Cai, contributed to design, data acquisition, analysis, and interpretation, drafted and critically revised the manuscript; M.F. Burrow, D.J. Manton, J.E.A. Palamara, contributed to conception, design, and data interpretation, critically revised the manuscript. All authors gave final approval and agree to be accountable for all aspects of the work.

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Declaration of Conflicting Interests

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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