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Dry bonding to dentin: Broadening the moisture spectrum and increasing wettability of etch-and-rinse adhesives

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ABSTRACT

Objective. To determine whether the effect of dentin moisture on the etch-and-rinse bonding may be minimized by dry-bonding protocols utilizing aqueous or ethanolic dimethyl sulfoxide (DMSO) pretreatments.

Methods. H_3PO_4-etched mid-coronal dentin surfaces from human molars were randomly blot- or air-dried for 30 s and pretreated with DMSO/H_2O or DMSO/EtOH solutions. Untreated samples served as control. Moisture control was performed by either blot- or air-drying. Samples were bonded with a multistep etch-and-rinse adhesive. Restored crown segments (n = 8/group) were stored in distilled water for 24 h and sectioned for microtensile bond strength testing. Resin-dentin beams (0.8 mm^2) were tested under tension until fracture (0.5 mm/min) after 24 h and two years of storage in artificial saliva at 37 °C.

SEM nanoleakage evaluation was performed on aged samples. Collagen wettability was also measured by sessile drops of the hydrophilic and hydrophobic bonding resins (n = 8/group). Data were examined by factorial ANOVA followed by the Tukey test ($\alpha = 0.05$).

Results. Dry bonding to untreated collagen produced inferior immediate and long-term bond strengths than wet bonding ($p < 0.05$). Regardless of initial hydration and moisture control, DMSO-dry bonding produced initially higher and stable bond strengths after aging ($p < 0.05$). DMSO-pretreated groups presented improved collagen wettability with lower silver uptake ($p < 0.05$).

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Significance. Despite the common belief that etch-and-rinse adhesives must be applied onto moist collagen, DMSO-dry bonding protocols not only improved bonding performance and hybrid layer integrity, but also brought more versatility to collagen hybridization by reducing overdrying-related issues.

1. Introduction

Resin-dentin bonding has greatly evolved in the past decades in search for more durable interfaces. Nevertheless, bonding to the biologically active dynamic dentin substrate still presents several unsolved challenges [1]. Dentin is an intrinsically hydrated mineralized tissue that imposes several obstacles to long-term resin bonding.

The two main factors involved in etch-and-rinse bonding are adequate wetting of the dentin surface by the adhesive components and subsequent micromechanical interlocking of resin monomers to the demineralized collagen fibrils upon curing [1,2]. To do so, maintenance of collagen interfibrillar spaces is critical for proper monomer penetration [1,3–5]. There is a general consensus that by maintaining a state of hydration previously to adhesive application, collagen interfibrillar spaces are preserved and thus improved bonding outcomes are achieved [6–8]. This was referred to as the wet-bonding technique [9] and it has been the standard protocol for etch-and-rinse bonding for the past three decades [1,4,5]. However, control of dentin moisture prior to adhesive application is not a simple procedure [6,10]. Optimal dentin moisture degree varies among different adhesive systems depending on their solvent composition [8,11], making proper clinical use of the wet bonding technique even more challenging. In addition, controlling dentin moisture in a reproducible manner is virtually impossible by current means, which further complicates the proper use of such technique-sensitive wet-bonding approach [1].

The high sensitivity of etch-and-rinse systems to dentin moisture, including both overwet and overdry conditions, strongly affects adhesive performance [12–14]. Detrimental effects of excessive water on the formation of highly cross-linked polymer chains [15,16] within hybrid layers contribute to the unpredictability and complexity of the wet-bonding approach [17]. Water entrapment within the collagen matrix limits the diffusion of cross-linking hydrophobic monomers deeply into hybrid layers [18], while phase separation is also likely to occur [8]. Monomer conversion may also be negatively affected by excessive residual moisture resulting in mechanically weaker polymers [19]. Even with theoretically ideal moisture conditions, wet-bonded interfaces are still prone to degradation over time [6,20]. Furthermore, residual water may also participates in collagen hydrolyses by endogenous enzymes (*i.e.* matrix metalloproteinases and cysteine cathepsins) [21,22] contributing to long-term resin-dentin bond degradation. Reduction or even elimination of such water-content benefits resin-dentin bonding [10,17,23,24], as long as collagen hybridization and polymer formation is not be jeopardized [25,26].

Undoubtedly, a simpler alternative to standardize dentin moisture and potentially reduce the detrimental effects of water entrapment would be the classic dry-bonding approach. The inability of resin-solvent blends to re-expand dried-collapsed collagen limits the dry-bonding approach [3,25]. Several attempts have been proposed to overcome such limitations and reestablish the dry-bonding approach with various degree of success [17,23,27–30]. Recently, dimethyl sulfoxide (DMSO) has emerged in the field of adhesive dentistry as a polar aprotic solvent capable of improving different aspects in resin-dentin bonding. Unlike previously proposed attempts, DMSO may simultaneously act in several fronts to facilitate dry bonding to dentin conventionally etched with H_3PO_4. Higher monomer diffusion [31], better hybrid layer formation [24,31,32] and even lower endogenous collagenolytic activity [23,33] have been attributed to DMSO. DMSO-dry bonding protocols are not only effective to produce higher initial bond strengths [24,34], but they preserve long-term bond strengths producing interfaces with lower levels of residual water [23,24]. Nonetheless, the necessity to re-wet air-dried collagen with DMSO pretreatments prior to hybridization raises concerns about the true ability to bond methacrylate monomers to dry and fully demineralized collagen. The combination of both collagen re-expansion by water-based DMSO pretreatments [35] and their ability to subsequently stiffen collagen [34] may confer dimensional stability to demineralized collagen fibrils. This could allow collagen air-drying at different bonding stages before adhesive application. The possibility to air-dry fully demineralized collagen before or after DMSO pretreatments would constitute a pivotal modification, characterizing a dry-bonding technique more realistic, reliable and reproducible. Moreover, the proposed disruption of residual-water layers surrounding collagen fibrils by DMSO [32,36] could further facilitate the infiltration of hydrophobic monomers in such dry state to strengthen hybrid layers.

Therefore, the primary aim of this study was to investigate the possibility of air-drying etched dentin as the sole form of moisture control in attempt to reduce moisture-related issues of resin-dentin bonding. This would discard the current necessity of maintaining etched dentin moist to preserve demineralized collagen interfibrillar spaces prior to hybridization. The objectives were to determine the effect of DMSO pretreatments and the degree of collagen moisture, prior and after pretreatments, on the long-term bond strength, hybrid layer quality and collagen wettability of a water-based three-step etch-and-rinse adhesive system. The tested null hypotheses were that conventional dry bonding and the pro-

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posed variations in DMSO-dry bonding approach would not affect: (i) resin-dentin bonding performance, (ii) hybrid layer integrity and (iii) collagen wettability of a water-based etch-and-rinse adhesive system.

2. Materials and methods

Extracted sound human third molars were obtained with informed consent from patients (18–26 years) under a protocol approved by the University of Oulu, Finland (#23-2003) in accordance with local regulations. Indications for tooth extractions were not related to the present study. After extractions, teeth were stored at 4 °C in 0.9% NaCl containing 0.02% NaN_3 to prevent microbial growth and were used within 1 month.

2.1. Experimental design and bonding procedures

The experimental design was composed of four study factors defined as: (i) initial collagen hydration condition at two levels (wet or dry bonding); (ii) dentin pretreatments at three levels (no pretreatment, DMSO/H_2O and DMSO/EtOH); (iii) collagen moisture condition prior to hybridization at two levels (blot- or air-drying) and (iv) storage time at two levels (24 h and 2 years). Control groups received no DMSO pretreatments following the conventional wet- or dry-bonding approaches tested at both storage times. Teeth were coronally sectioned under water-cooling to expose flat midcoronal dentin surfaces using a slow speed diamond saw (Isomet, Buehler Ltd, Lake Bluff, IL, USA). Absence of remaining enamel on the dentin surfaces was verified with a stereomicroscope (Leica M60, Leica Microsystems, Wetzlar, Germany) at 40× magnification. Roots were removed 1 mm below the cervical line and discarded. Exposed dentin surfaces were wet polished with 320-grit SiC paper for 60 s for smear layer standardization. Crown segments (n = 8/group) were randomly allocated to 10 groups according to dentin condition prior to hybridization, dentin pretreatments and moisture control after pretreatments. Dentin surfaces were etched for 15 s with 32% phosphoric acid (Scotchbond Universal Etchant, 3 M ESPE, St. Paul, MN, USA), rinsed for 30 s and either blot-dried, leaving the surface partially wet (moist dentin), or air-dried for 30 s (dry dentin). The 50% DMSO (v/v) solutions were prepared by mixing equal volumes of DMSO (Dimethyl Sulfoxide, Sigma-Aldrich, St. Louis, MO, USA) in distilled water or ethanol (Ethanol 99.8%, Sigma-Aldrich). 50 μL of DMSO/H_2O or DMSO/EtOH solutions [23,31,32] were actively applied on the etched-dentin surfaces for 60 s. Moisture control was performed by either blot-drying, until paper filters presented no visible moisture or by air-drying for 30 s [23,31,32]. One water-based three-step etch-and-rinse adhesive (Scotchbond Multi-Purpose: SBMP, 3 M ESPE) was used following manufacturer's instructions. SBMP's *Primer* was applied for 10 s and gently evaporated for 10 s with air-streams. The *Bond* was subsequently applied and gently air-blown for 5 s to produce a more uniform adhesive layer. Both were actively applied with manual light pressure of approximately 4 g, equivalent to a slight rubbing pressure [10,37]. Adhesive procedures were carried out in a controlled environment with a temperature of 24 °C and a relative humidity of 45–55%. Adhesives were light cured for 10 s using a LED light-curing unit (Elipar Deepcure, 3 M ESPE) at 1200 mW/cm^2. Composite blocks were built with a nanofilled composite resin (Filtek Z350, 3M ESPE) in two increments of 2 mm. Each increment was light-cured for 20 s. All bonding procedures were carried out by a single operator. The restored crown segments were stored in distilled water for 24 h at 37 °C to allow water sorption and postoperative polymerization. Resin–dentin beams were produced with a cross-sectional area of approximately 0.8 mm^2 by sectioning the restored crowns longitudinally in mesio-distal and buccal-lingual directions perpendicular to the bonded interface with a slow-speed diamond saw (Isomet, Buehler Ltd). A minimum of 18 resin-dentin beams were produced per tooth.

2.2. Resin-dentin beam storage

Resin-dentin beams were randomly selected for the microtensile test under two conditions: immediate testing after 24 h of storage in distilled water at 37 °C and long-term aging after two-years in artificial saliva (pH 7.4) at 37°C composed by 5 mM HEPES, 2.5 mM $CaCl_2$·H2O, 0.05 mM $ZnCl_2$, and 0.3 mM NaN_3 [38]. The storage media was changed biweekly to prevent possible pH changes. In order to obtain a research design balanced by tooth dependency [39], resin-dentin beams from the same tooth were submitted to both testing periods (*i.e.* 24 h and 2 years). For the nanoleakage evaluation, resin-dentin beams aged for 2 years were selected to focus on the effect of aging on hybrid layer integrity.

2.3. Microtensile bond strength (μTBS)

Microtensile bond strength evaluation followed the Academy of Dental Materials guidelines for non-trimmed μTBS testing [39]. A minimum of 7 beams per tooth (n = 8 teeth/group) were tested on each storage period. Beams were individually attached to a custom-made testing jig using a cyanoacrylate adhesive (Loctite 416, Henkel Corp., Dublin, Ireland) and tested under tension on a mechanical testing machine (Bisco, Schaumburg, IL, USA) at a crosshead speed of 0.5 mm/min until failure to obtain the maximum load (*P*) in N. The cross-sectional area (*CA*) in mm^2 of each beam was measured with a digital caliper to nearest 0.01 mm. The formula $\mu TBS = P/CA$ was used to calculate μTBS values in MPa. Pre-test failures were considered as 0 MPa for the statistical analyses. Since tooth was considered as the statistical unit, bond strengths of resin-dentin beams from each tooth, tested at each period, were averaged to represent the bond strength of each tooth [39]. Both surfaces of fractured resin-dentin beams were analyzed with a stereomicroscope (Leica MD60, Leica Microsystems) at 40× magnification to determine fracture patterns. Unidentifiable samples were examined by scanning electron microscopy (SEM) (Phenom ProX, Phenom-World, Eindhoven, Netherlands). Fracture modes were classified as cohesive (failure exclusive within dentin or resin composite), adhesive failure (failure at resin/dentin interface) and mixed failure (failure at resin/dentin interface with cohesive failure of the neighboring substrates).

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2.4. Nanoleakage evaluation

Three resin-dentin beams per tooth (n = 8/group) stored for 2 years in artificial saliva were randomly selected to measure silver nitrate uptake at the bonded interface after long-term storage. Nanoleakage evaluation was performed according to a protocol previously described by Tay et al. [40]. Briefly, resin-dentin beams were initially wet polished with 2000-grit SiC paper and coated with two layers of nail varnish applied up to 1 mm of the bonded interfaces. After rehydration in distilled water for 1 h, beams were immersed in 50% (w/v) ammoniacal silver nitrate (pH 9.5) for 24 h and thoroughly rinsed in distilled water for 120 s. Subsequently, samples were immersed in photo-developing solution (Kodak Professional D-76 developer, Kodak Rochester, NY, USA) for 8 h under a fluorescent light to reduce silver ions into metallic silver grains. Beams were embedded in epoxy resin, wet polished with 600-, 1000-, and 2000-grit SiC paper (Carbimet, Buehler Ltd.,) and 1, 0.25 (MetaDi, Buehler Ltd) and 0.05 μm (MasterPrep, Buehler Ltd) polishing pastes. Embedded samples were ultrasonically cleaned in distilled water after each polishing step for 5 min, air-dried for 2 h, mounted on aluminum stubs, dried in silica overnight and carbon sputtered. Nanoleakage extension was qualitatively analyzed using SEM imaging on backscattering mode at 10 kV (Phenom ProX, Phenom-World). Silver uptake patterns and extensions were blindly evaluated by an experienced operator at magnifications ranging from 1000−10000×.

2.5. Contact angle measurements

Dentin discs measuring approximately 2.5 mm in thickness (n = 8/group) from the midcoronal section of sound third molars were transversally sectioned under water cooling (Isomet, Buehler Ltd). Occlusal surfaces were inspected for the absence of remaining enamel with a stereomicroscope (Leica M60, Leica Microsystems) at 40× magnification and polished with 600-grit SiC paper for 60 s. H_3PO_4-etching (Scotchbond Universal Etchant, 3 M ESPE) was performed for 15 s and rinsed for 30 s. Moisture control and DMSO pretreatments were performed as previously described for the bond strength measurements. In order to investigate the wettability properties, contact angle measurements were performed using the sessile drop method. Dentin discs were placed on top of a water droplet and a goniometer (Attension Thetha Lite 101, Biolin Scientific, Espoo, Finland) was used to measure contact angles of the hydrophilic (Primer, Scotchbond Multi-Purpose: SBMP, 3 M ESPE) and hydrophobic (Bond, Scotchbond Multi-Purpose: SBMP, 3 M ESPE) bonding resins. Droplets (approximately 3 μL) were deposited on the etched-dentin surfaces with a micropipette after the respective dentin pretreatments and drying conditions. Contact angles θ were measured up to 240 s after the drop. Images were captured at 0.1 s intervals during the initial 20 s, 0.5 s during the subsequent 20 s and after 5 s intervals for the remaining 200 s to evaluate spreading times. Left and right contact angles were automatically averaged by the goniometer software (OneAttension Version 2.9 (r5612), Biolin Scientific, Finland). A logarithmic fitting model [41] of the contact angles over time was used to calculate the spread rate constant k for the bonding resins according to DMSO pretreatments and moisture conditions.

2.6. Statistical analysis

Bond strength data were normally distributed (Shapiro-Wilk; $p = 0.2$) and homoscedastic (Levene Test; $p = 0.24$). Four-way ANOVA followed by the Tukey test were employed with statistical significance set at $\alpha = 0.05$ using IBM SPSS Statistics for Windows, version 26 (IBM Corp., Armonk, NY, USA.

3. Results

3.1. Microtensile bond strength test

The mean cross-sectional area of the resin-dentin beams (0.81 ± 0.1 mm^2) ranged from 0.72 to 0.89 mm^2 without significant differences between groups regarding specimen size (p = 0.251). Four-way ANOVA showed that "initial collagen hydration" ($p < 0.0001$; $\eta_p^2 = 0.263$), "dentin pretreatments" (p = 0.0001; $\eta_p^2 = 0.871$), "collagen moisture prior to hybridization" ($p = 0.0001$; $\eta_p^2 = 0.045$) "storage time" ($p = 0.0001$; $\eta_p^2 = 0.164$), the interactions between "initial collagen hydration * dentin pretreatments" ($p = 0.0001$; $\eta_p^2 = 0.341$) and "dentin pretreatment * storage" ($p = 0.0001$; $\eta_p^2 = 0.246$) significantly affected bond strengths. Resin-dentin bond strength values are shown in Fig. 1 and Table 1. Dry bonding produced significantly lower immediate bond strength (approximately -48%) compared to the traditional wet bonding approach. Irrespective of initial dentin hydration (wet or dry) or moisture control (blot- or air-drying), DMSO pretreatments produced significantly higher bond strengths (ranging from 30% to 45%) compared to the traditional wet bonding protocol. No significant differences were detected between DMSO pretreated groups. Aging produced significant reductions (approximately −40%) in samples following the traditional wet bonding protocol. Dry bonding presented the lowest bond strengths after aging with a significant reduction of −85%. No significant changes were observed for the DMSO pretreated groups after aging irrespective of initial dentin hydration or moisture control. Fracture pattern distributions for all groups are shown in Fig. 2. At 24 h, the predominant pattern was mixed, except for the dry-bonded samples, which were mostly characterized by adhesive failures. After aging, samples bonded following the wet bonding protocol presented adhesive failures as the predominant pattern. Aged dry-bonded samples presented 71% pretest failures. Aged DMSO pretreated samples did not present substantial changes in fracture patterns compared to samples tested at 24 h.

3.2. Nanoleakage evaluation

Representative SEM micrographs of silver uptake and nanoleakage patterns for all groups after long-term aging are shown in Fig. 3. Nanoleakage was invariably identified at the peritubular region around resin tags in all groups with no marked differences in their extension between DMSO treatments. Different nanolekage patterns between the control and DMSO-pretreated groups were identified within the hybrid layer. Dry-bonded control samples presented the highest levels of silver uptake, with the hybrid layers nearly fully impregnated by heavy silver deposits, depicting extremely

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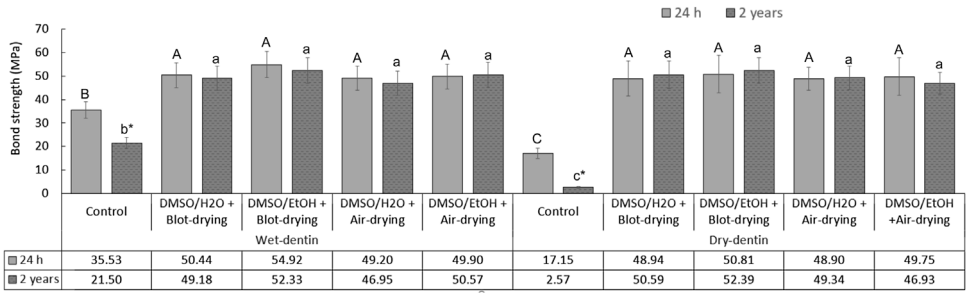

	Wet-dentin					Dry-dentin				
	Control	DMSO/H2O + Blot-drying	DMSO/EtOH + Blot-drying	DMSO/H2O + Air-drying	DMSO/EtOH + Air-drying	Control	DMSO/H2O + Blot-drying	DMSO/EtOH + Blot-drying	DMSO/H2O + Air-drying	DMSO/EtOH +Air-drying
24 h	35.53	50.44	54.92	49.20	49.90	17.15	48.94	50.81	48.90	49.75
2 years	21.50	49.18	52.33	46.95	50.57	2.57	50.59	52.39	49.34	46.93

Fig. 1 – Microtensile bond strength (MPa) means and standard deviations of resin-dentin interfaces bonded to wet or dry dentin using aqueous or ethanolic DMSO solutions as pretreatments. Moisture control after pretreaments was performed by blot- or air-drying. Samples were tested at 24 h or after 2 years of aging in artificail saliva at 37 °C. Tooth was considered the statiscial unit (n = 8/group). Different upper case letters indicate significant differences beween groups within the 24 h testing period. Different lower case letters indicate significant differences beween groups after aging for 2 years. * inidicates significant differences between aging periods within similar treatments. Statistical comparisons were performed by the Tukey test (α = 0.05).

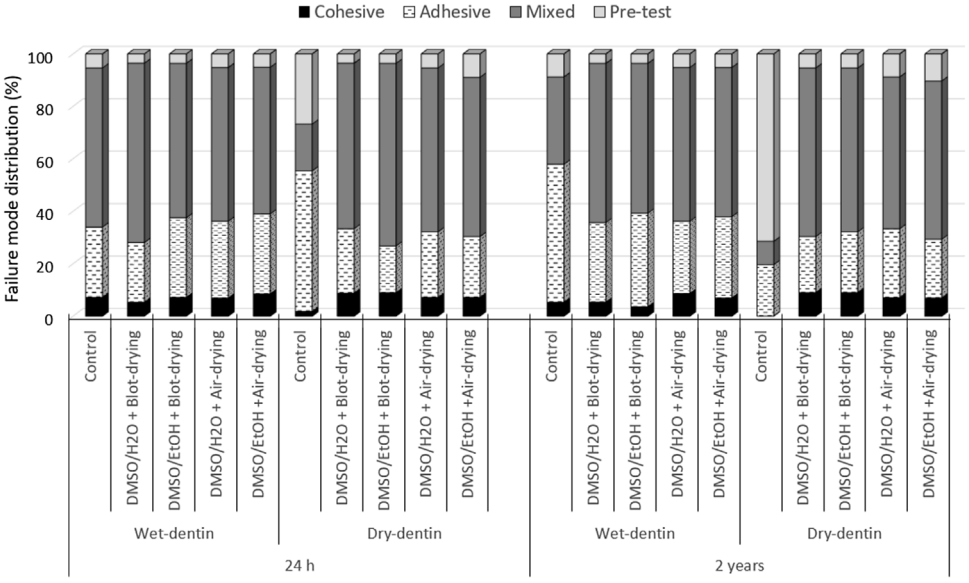

Fig. 2 – Fracture patterns in percentages (%) of tested specimens after the bond strength test at 24 h and 2 years of aging in artificail saliva at 37 °C. Resin-dentin interfaces were created by bonding a multistep etch-and rinse adhsieve (SBMP) to wet or dry dentin, using DMSO pretreatments with different moisture controls (blot- or air-drying). Fracture patterns were classified as: cohesive failure = failure exclusive within dentin or resin composite; adhesive failure = failure at resin/dentin interface and mixed failure = failure at resin/dentin interface with cohesive failure of the neighboring substrates.

porous bonded interfaces. Wet-bonded control samples presented lower extensions of silver deposits compared to dry-bonded samples. Nanoleakage patterns were characterized by reticular silver deposits extending mainly at the bottom of the hybrid layers. Areas of complete silver uptake through the full thickness of the hybrid layer were also observed, but to a much lesser degree than in the dry-bonded samples.

Irrespective of the initial dentin hydration (wet or dry) or moisture control (blot- or air-drying) after DMSO pretreatments, both pretreatments (DMSO/H_2O and DMSO/EtOH) produced clearly lower levels of silver uptake at the bonded interfaces compared to the wet and dry control groups. Nanoleakage extensions were similar in DMSO-pretreated groups, characterized by spotted silver deposits sparsely distributed across the hybrid layers. Areas with complete hybrid layer silver impregnation were hardly identified within DMSO-pretreatment dentin.

3.3. *Contact angle measurements*

A rapid decrease in contact angles for both bonding resins occurred during the initial 5 s, followed by a slower but still considerable decrease rate until 20 s. Contact angles then decreased slowly and reached a nearly constant value at approximately 180 s for the hydrophobic resin and 210 s for the hydrophilic resin. Fig. 4 illustrates the variation in contact angles over time observed for both resins applied on the flat dentin surfaces submitted to the different DMSO treatments with different moisture conditions. Contact angles from each

Table 1 – Microtensile bond strength means (MPa), standard deviations (±SD) and fracture modes.

	Wet dentin				Dry dentin			
	Control	DMSO/H_2O +Blot	DMSO/EtOH +Blot	DMSO/H_2O +Air	DMSO/EtOH +Air	Control	DMSO/H_2O +Blot	DMSO/EtOH +Blot	DMSO/H_2O +Air	DMSO/EtOH +Air
24 h	35.53 ± 3.50 (4/15/34/ 3/56)	50.44 ± 5.35 (3/13/39/2/ 57	54.92 ± 5.49 (4/17/33/2/ 56	49.20 ± 5.16 (5/17/36/2/ 60	49.90 ± 5.29 (6/19/34/2/ 61	17.15 ± 2.21 (1/30/10/15/ 56)	48.94 ± 7.50 (5/14/36/2/ 57	50.81 ± 8.02 (5/10/41/2/ 58	48.90 ± 4.97 (4/14/35/3/ 56	49.75 ± 7.96 (4/13/34/5/ 56
2 years	21.50 ± 2.24 (3/30/19/5/ 57)	49.18 ± 5.17 (3/17/34/2/ 56	52.33 ± 5.41 (2/20/33/3/ 58	46.95 ± 5.16 (5/16/34/3/ 58	50.57 ± 5.32 (4/18/33/3/ 58	2.57 ± 0.34 (0/11/5/40/ 56)	50.59 ± 5.75 (5/12/38/3/ 58	52.39 ± 5.41 (4/13/36/3/ 56	49.34 ± 5.02 (5/13/35/3/ 56	46.93 ± 4.59 (4/13/35/6/ 58

Tooth was considered the statistical unit (n = 8). Numbers in parentheses represent the total number of specimens following the fracture mode classification (1/2/3/4/5): (1) cohesive failure; (2) adhesive failure; (3) mixed failure; (4) pre-test failure and (5) total number of tested specimens.

group followed a logarithmic decay model, allowing the determination of the kinetics parameters listed as the spreading rate constants during the initial 20 s in Table 2. Factorial ANOVA showed that the factors "initial collagen hydration" ($p < 0.0001$; $\eta_p^2 = 0.19$), "dentin pretreatment" ($p < 0.0001$; $\eta_p^2 = 0.601$), "collagen moisture prior to hybridization" ($p < 0.0001$; $\eta_p^2 = 0.152$), "resin" ($p < 0.0001$; $\eta_p^2 = 0.54$), "time" ($p < 0.0001$; $\eta_p^2 = 0.77$) and the interactions "dentin pretreatment * resin * time" ($p < 0.017$; $\eta_p^2 = 0.77$), "dentin pretreatment * collagen moisture prior to hybridization * resin" ($p < 0.002$; $\eta_p^2 = 0.27$) significantly affected the contact angles. For the control groups, the hydrophilic resin produced significantly lower contact angles on wet than on dry dentin at both time periods (0.1 s and 20 s). In contrast, the hydrophobic resin presented no significant differences between wet-untreated or dry-untreated dentin at the same time periods. The hydrophobic resin produced significantly higher contact angles (roughly 90%) than the hydrophilic resin when deposited on untreated dentin at 0.1 s. Similarly at 20 s, hydrophobic resins also produced higher contact angles than the hydrophilic resin (roughly 85% higher) under wet conditions; however, no significant differences between resins occurred on air-dried dentin at 20 s. For the hydrophilic resin, DMSO pretreatments produced significantly lower contact angles than their respective dry-control group on both time periods irrespective of the initial collagen hydration (wet or dry) or moisture control (blot- or air-drying). Such contact angles were not statistically different from their respective wet-control group. Unlike the hydrophilic resin, the hydrophobic resin produced significantly lower values on DMSO-pretreated collagen when compared to their respective dry- and wet-control groups. These significant reductions were in the order of 30–50% at both time periods and occurred regardless of the initial dentin hydration (wet or dry) or moisture control (blot- or air-drying).

4. Discussion

Since dry bonding negatively affected resin-dentin bond strengths and hybrid layer stability while DMSO-dry protocols improved bonding, the first hypothesis was rejected. Bonding a three-step etch-and-rinse adhesive system to air-dried dentin produced inferior outcomes compared to the traditional wet-bonding technique, which is in accordance with previous reports [10,25,28,42]. Our findings reinforce the concept that etch-and-rinse adhesives must be preferably bonded to moist dentin to avoid collagen collapse and thus minimize issues related to matrix shrinking [3]. The main problem with dry bonding resides on collagen collapse, an active and rapid process involving the rapid spontaneous development of hydrogen bonds between adjacent collagen peptides and decreasing interfibrillar spaces [3]. Solvents may fully (*i.e.* water) or partially (*i.e.* ethanol, propanol, and acetone) re-expand collapsed collagen depending on whether their hydrogen bonding solubility parameters (δh) exceed 14.8 $(J/cm^3)^{1/2}$ [3]. Methacrylate-based bonding agents do not always promote adequate re-expansion of dried collagen [3]. As a result, diffusion of methacrylate monomers through such densely-packed collagen meshes is inefficient [3], which greatly compromises dentin bonding [10,28,42]. When com-

Table 2 – Wettability kinetics of hydrophilic (Primer) and hydrophobic (Bond) resins deposited onto DMSO-pretreated dentin with different moisture levels: contact angles at 0 s, 20 s, 240 s, standard deviation and spreading rate constant (*k*) at the initial 20 s.

Resin	Initial dentin condition	Dentin pretreatment	Moisture control (drying)	0.1 s	20 s	*k*
Hydrophilic (*Primer*)	Wet	(control)	Blot	23.2 (3.3) ^{CD}	13.1 (2.1) ^{CD}	1.85
	Dry	(control)	Air	30.5 (3.4) ^{B}	20.9 (3.2) ^{B}	1.71
	Wet	DMSO/H_2O	Blot	16.9 (2.9) ^{D}	9.9 (1.9) ^{D}	2.98
			Air	21.6 (4.9) ^{D}	12.4 (2.7) ^{D}	3.29
		DMSO/EtOH	Blot	16.8 (3) ^{D}	10.6 (4.3) ^{D}	2.23
			Air	18.9 (2.9) ^{D}	12.6 (3.8) ^{D}	2.7
	Dry	DMSO/H_2O	Blot	18.3 (3.9) ^{D}	11.9 (3.6) ^{D}	2.34
			Air	22.1 (3.4) ^{D}	11.8 (3.7) ^{D}	2.93
		DMSO/EtOH	Blot	18.8 (3.7) ^{D}	11.3 (3.1) ^{D}	2.27
			Air	20.8 (3.3) ^{D}	11.2 (2.3) ^{D}	2.21
Hydrophobic (*Bond*)	Wet	(control)	Blot	44.1 (5.3) ^{A}	24.3 (3.6) ^{A}	3.62
	Dry	(control)	Air	45.5 (3.4) ^{A}	22.4 (3.1) ^{AB}	3.98
	Wet	DMSO/H_2O	Blot	28.3 (3.5) ^{BC}	15.5 (3.4) ^{C}	4.99
			Air	30.3 (6.7) ^{B}	16.1 (3.4) ^{C}	4.64
		DMSO/EtOH	Blot	22.4 (3.5) ^{CD}	10.2 (1.6) ^{D}	4.65
			Air	30.7 (3.5) ^{B}	11.1 (3.6) ^{D}	5.22
	Dry	DMSO/H_2O	Blot	28.3 (4.3) ^{BC}	14.7 (3.1) ^{C}	4.93
			Air	30.8 (3) ^{B}	16.4 (1.9) ^{C}	5.7
		DMSO/EtOH	Blot	24.1 (4.1) ^{C}	10.6 (1.8) ^{D}	4.5
			Air	30.3 (5.1) ^{B}	14 (1.5) ^{CD}	4.34

Contact angles with different superscript letters indicate significant difference according to Tukey test ($p < 0.05$) when analyzed per column.

bined with HEMA, the re-expansion potential of solvents tends to drop, except for HEMA-water mixtures [3,43,44]. HEMA-water mixtures, commonly found in commercial bonding resins [45], may re-expand dried collagen up to 92%; however, subsequent solvent evaporation substantially shrinks the matrix again [44]. Water evaporation results in interpeptide hydrogen bonding, which may expel HEMA from within the collagen matrix [46]. Such instability of the collagen matrix prevents optimal resin-dentin bonding. Although HEMA-water mixtures may re-expand dried collagen quite effectively [3,43,44], additional resources, such as vigorous adhesive application, are necessary to produce similar outcomes to wet bonding [10].

The antagonic effects of water on resin-dentin bonding have been well documented [3,5,13]. While the lack of moisture compromises interfibrillar spaces, excess moisture may be detrimental to polymer formation [15]. Etch-and-rinse adhesives present a small window of opportunity regarding optimal surface moisture [6,11]. It is virtually impossible to consistently determine the ideal surface moisture in a clinical situation. Hence, broadening the moisture spectrum of etch-and-rinse adhesive systems to substantially drier levels would not only prevent potential problems associated to overwetting, but also allow a more consistent moisture control. Air-drying is a far simpler and more consistent moisture control approach if compared to blot-drying. The safe use of air-drying could greatly facilitate bonding procedures of etch-and-rinse bonding. Since comparable bond strength results were obtained on wet or dry collagen, regardless of initial dentin hydration or moisture control, it is evident that DMSO pretreatments eliminated the negative short and long-term effects of air-drying on resin-dentin bonding.

The benefits of using DMSO solutions as dentin pretreatments have been previously reported for wet [31,32,47] and air-dried [23,24] collagen. Our previous studies regarding DMSO-dry bonding [23,24,34] also made use of extensive air-drying for resin-dentin bonding to aid in the reduction of water content within the bonded interface. Nonetheless, DMSO pretreatments were blot-dried before adhesive application to avoid possible problems with collagen collapse after the application of DMSO pretreatments. In the present study, prolonged air-drying before or after DMSO pretreatments had no negative effects on bond strengths of etched dentin. DMSO-pretreated collagen may be blot- or extensively air-dried immediately before adhesive application without any negative effect on long-term bond strengths. This brings new possibilities to facilitate DMSO-bonding protocols and to reduce residual water from hybrid layers more efficiently by air-drying DMSO-pretreated collagen. Noteworthy, residual water is more effectively removed from collagen matrixes prior to the addition of bonding resins containing HEMA [48]. Hydrogen bonding between water and methacrylate monomers hinders effective water removal by evaporation [49]. In theory, prolonged air-drying after DMSO-pretreatments could potentialize water removal from hybrid layers. In previous attempts to combine DMSO and dry bonding, the pretreatment solutions were blot dried [23,24] to prevent possible collagen collapse as proposed for the ethanol-wet bonding technique [3]. It is important to note that saturation of demineralized dentin with polar organic solvents tends to stiffen collagen [50–52]. DMSO is a polar aprotic solvent with considerably low vapor pressure [53]. We speculate that DMSO-pretreated collagen may present sufficient increase in stiffness to prevent collagen collapse following prolonged air-drying [34], without any comprise in polymer formation. Unlike ethanol, which readily evaporates from collagen after air-drying, DMSO's low vapor pressure prevents full evaporation. Residual DMSO molecules may contribute to the maintenance of interfib-

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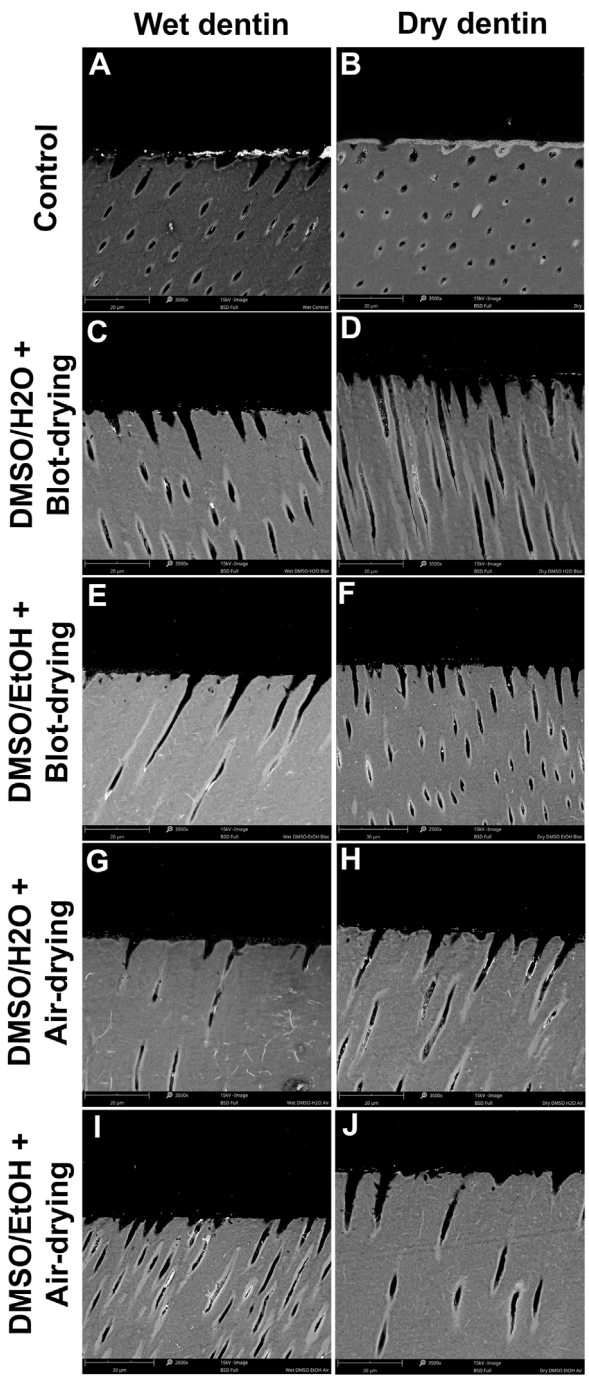

Fig. 3 – Representative SEM nanoleakage micrographs of aged resin-dentin interfaces bonded to wet or dry dentin using aqueous or ethanolic DMSO solutions as pretreatments. Moisture control after the application of pretreaments was performed by blot- or air-drying.

rillar spaces allowing appropriate monomer diffusion even after prolonged air-drying. Reduction of the post-collapsing effect of solvent volatilization could explain the higher bond strengths produced by DMSO pretreatments. Further studies should validate this hypothesis.

The rationale for testing different moisture controls (blot- and air-drying) at different stages (before or after pretreatments) was to determine whether DMSO-dry bonding would be possible and to identify which combinations would produce the most favorable long-term outcomes. Surprisingly, the initially higher bond strengths produced by bonding protocols containing DMSO were not affected by long-term aging irrespective of moisture controls at the different drying stages. Since the hybrid layer integrity was substantially improved in DMSO-pretreated samples after aging and bonded interfaces created on dry-untreated collagen were extremely porous, the second null hypothesis was rejected. DMSO-pretreatments not only improved bond strengths, but also produced hybrid layers with lower porosity after aging regardless of moisture control. This highlights the ability of DMSO-pretreatments to reduce technique sensitivity of resin bonding on etched dentin by broadening the spectrum of moisture towards a drier state. DMSO-water (δh 26.8 $(J/cm^3)^{1/2}$) and DMSO-ethanol (δh 16.6 $(J/cm^3)^{1/2}$) pretreatments present δh values superior to dry collagen (δh 14.8 $(J/cm^3)^{1/2}$). Although the overall expansion of dried collagen varies among solvents [3] and solvent mixtures [35], δh values higher than 14.8 $(J/cm^3)^{1/2}$ indicate the ability of both DMSO/H_2O and DMSO/EtOH to break interpeptide hydrogen bonds and thus re-expand collagen. DMSO/H_2O is clearly more effective in re-expanding dry collagen due to its higher δh. However, the use of water-free DMSO pretreatments further facilitates the overall removal of residual water from bonded interfaces. Furthermore, air-drying DMSO/EtOH from dentin surfaces may increase water removal as ethanol evaporates. Water evaporation is more efficient when performed before adhesive application [49]. Therefore, air-drying may potentialize water removal compared to routinely employed bonding protocols that rely exclusively on adhesive solvents to chase water molecules within demineralized collagen. To the best of our knowledge, this is the first attempt to successfully bond methacrylate monomers to demineralized collagen via ethanol saturation followed by extensive air-drying to eliminate solvents prior to adhesive application.

One of the first requirements for good adhesion is the optimum wettability of the bonding surface, allowing spontaneous spreading of the bonding agent on the surface. An intimate contact between the bonding agent and the surface is thereby of paramount importance to produce reliable bonding. A positive correlation exists between dentin wetting and bond strengths [54]. High wettability relates to intimate resin-dentin contact, which leads to enhanced adhesion. This is strongly dependent on the physicochemical parameters attributed to the bonding agent and the bonding surface such as chemical composition, viscosity, polarity, surface roughness and hydration. Measurement of contact angles of a liquid over a surface is the most common method to investigate wettability [41,54–56]. In this study, 20 s was established as a cutoff point, since most of the reduction in contact angles took place before this time point. In addition, 20 s is well within clinically acceptable time during bonding procedures. The rationale for measuring contact angles of the hydrophilic and hydrophobic resins separately was to determine the specific effects of the DMSO-bonding protocols on their wettability. Naturally, the hydrophobic resin produced higher contact angles than the hydrophilic resin on untreated dentin. Hydrophobic bonding resins contains higher ratios of high molecular weight

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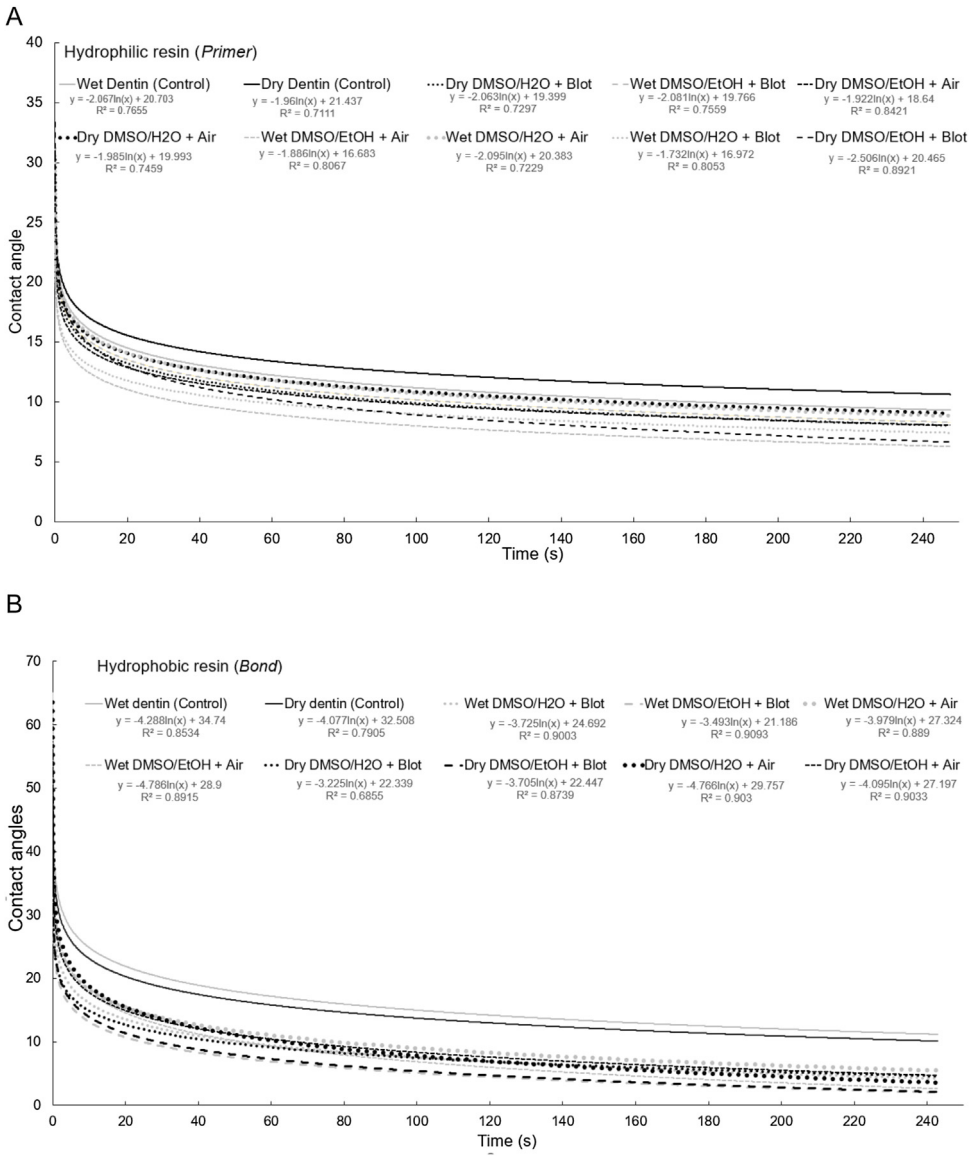

Fig. 4 – Contact angle evolution up to 240 s of hydrophobic (A; Bond) and hydrophilic (B; Primer) resins deposited onto wet or dry H_3PO_4-etched dentin pretreated with aqueous or ethanolic DMSO solutions followed by blot- or air-drying. Trend lines for each group (n = 8 measurements/group) were determined by the logarithmic decay model.

monomers [45]. Such cross-link monomers (*i.e.* bis-GMA) produce strong intermolecular hydrogen-bonding interactions between the hydroxyl groups (OH) and the carbonyl groups (C═O) in distinct bis-GMA monomers [57]. This accounts for the higher viscosity of the commoner, which reduces overall monomer mobility and consequently hinders collagen wetting. Moreover, dentin hydrophobicity increases with air-drying [56]. The notion that air-drying reduces the wettability of demineralized collagen was demonstrated over two decades ago [54–56] and further complicates resin-dentin bonding. Our bond strength data corroborates the latter. The high water content of the hydrophilic resin did not compensate for the lack of collagen moisture. Higher contact angles were observed for the HEMA-based hydrophilic primer on air-dried dentin collagen confirming the worse interaction between them [56].

Clinical adhesive procedures usually fall short of adequate resin spreading times [41,54,56], which compromises optimal resin-dentin wetting. This was corroborated by our findings where hydrophobic and hydrophilic resins achieved near equilibrium contact angles only at 180 and 210 s, respectively. From a clinical perspective, waiting for the bonding resins to completely wet dentin surfaces is unfeasible. The effect of DMSO on the specific spreading behavior of bonding resins onto collagen remained unknown until now. DMSO-pretreatments reversed wettability issues of air-dried collagen, so the third hypothesis was rejected. DMSO has the ability to reduce contact angles between water and dentin collagen [33,35], implying wettability improvements. Altogether, DMSO pretreatments accelerated resin spreading. Spreading rate constants (*k*) were 20–60% higher during the initial 20 s for DMSO-pretreated dentin. Regardless of initial dentin hydra-

tion (wet or dry) or moisture control (blot- or air-drying), DMSO increased wettability of the hydrophilic resin to levels similar to those of wet dentin, eliminating the negative impact of air-drying on collagen wetting. An even more profound effect was observed for the hydrophobic resin, with reductions in contact angles ranging from 30 to 50 % at 20 s. It is important to note that the lowest contact angles at 20 s occurred for ethanol-containing DMSO pretreatments. While DMSO pretreatments had no effect on contact angles of the hydrophilic resin applied on wet dentin, they greatly facilitated the spread of the hydrophobic resin on dry or wet collagen. Replacing water by ethanol, as the cosolvent in the pretreatment solution, had a positive impact in the wettability of the hydrophobic bonding resin. Water is generally poorer as a solvent for methacrylate monomers compared to ethanol, especially considering high molecular weight monomers such as bis-GMA present in hydrophobic formulations. It is tempting to speculate that priming of etched dentin with only DMSO-based cosolvents containing no hydrophilic monomers would be possible. Adhesive spreading indeed occurs simultaneously with monomer diffusion across demineralized collagen, albeit not necessarily at the same relative rate. The diffusion of high molecular weight monomers through dried-collapsed collagen is a demanding process, which may be facilitated by DMSO pretreatments. Nonetheless, more studies are necessary to evaluate both the feasibility and stability of resin-dentin bonded interfaces produced with a priming step free from hydrophilic monomers.

5. Conclusion

The ability to safely air-dry demineralized collagen and yet produce more stable resin-dentin bonding and less porous hybrid layers over time can be considered a major step towards technique-sensitive reduction of etch-and-rinse adhesive systems. DMSO not only improved long-term resin-dentin bonding, but also provided an added versatility to minimize overdrying-related issues in etch-and-rinse bonding. Moreover, the proposed DMSO-ethanol pretreatment followed by the air-drying approach constitutes a feasible alternative to reduce residual water from resin-dentin interfaces by broadening the moisture spectrum of demineralized dentin to drier levels without compromising collagen wettability.

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