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Bonding neat hydrophobic-rich resins to etched dentin: A proof of concept

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ABSTRACT

Objectives: To examine whether the effectiveness of current dentin-priming approaches requiring solvated hydrophilic resins may be replicated by modifying the infiltration dynamics of neat methacrylate-based monomers into dry-etched dentin using dimethyl sulfoxide (DMSO) pretreatments. *Methods:* H_3PO_4-etched mid-coronal dentin surfaces from human molars were air-dried for 30 s and randomly pretreated with 50 %(v/v) ethanolic DMSO for 20 or 60 s. Untreated samples and an isolated wet-bonding group served as controls. Samples were bonded with a three-step etch-and-rinse adhesive or simply with the solvent-free hydrophobic-rich resin. Restored crown segments (n = 7/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 failure (0.5 mm/min) after 24 h or 2 years of storage in artificial saliva at 37 °C. Nanoleakage evaluation and hybrid layer characterization were performed by SEM. Bond strength data was examined by three-way ANOVA followed by Tukey and Dunnett's test ($\alpha = 0.05$). *Results:* Pretreatments significantly affected the ability of neat and solvated resins to bond to etched-dry dentin ($p = 0.001$). Ageing significantly lowered bond strengths depending on resin composition and DMSO-application times ($p = 0.007$). While hybridization of DMSO-treated dentin with the solvated resin produced no significant reductions in bond strengths after ageing ($p < 0.05$) improving hybrid layer integrity, direct bonding of the neat hydrophobic-rich resin matched the long-term bonding performance of the "gold standard" wet-bonding protocol ($p > 0.05$). *Significance*: Lowering dentin's hydration state via DMSO-dry bonding allows direct coupling of neat methacrylate-based resins, which may contribute to developing new strategies to ultimately extend the durability of resin-dentin interfaces.

1. Introduction

Resin-dentin bonding mechanisms strongly rely on hydrophilic-based approaches to produce favorable clinical outcomes [1]. The intrinsic moist nature of dentin [2] endorses the consensus that hydrophilic comonomers solvated in organic polar solvents or in water remain critical to promote acceptable bonding. Although a great body of evidence has shown favorable clinical and laboratorial outcomes for contemporary dental adhesives [1], relying on bonding resins with high water affinity [3,4] has raised concerns for decades [5,6]. Hydrophilic domains created at hybrid layers are unstable and highly susceptible to long-term degradation [1,7,8]. Water sorption [9] and hydrolysis-induced degradation [1,7,8] impair the mechanical properties of bonded interfaces [10] contributing to failure. Hence, rendering bonding resins less hydrophilic is imperative for genuine advances in adhesive dentistry.

Dentin's morphology, however, hinders the possibility of "true" hydrophobic bonding via conventional protocols [5]. Current adhesive protocols rely on hydrophilic comonomers and "water-chasing" solvents [6] to enhance dentin wetting and reduce phase separation of dental adhesives containing high-molecular weight hydrophobic dimethacrylates when in contact with water [11]. Incorporation of solvents into resin blends lower the viscosity of methacrylate-based resins. This is critical to promote adequate micromechanical interlocking, especially in

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etch-and-rinse adhesives [12,13]. The use of volatile organic polar solvents and/or water is indispensable in the formulation of dental adhesives [1,13]. Nonetheless, complete solvent evaporation before light-curing is hardly achieved [14]. Residual solvents can jeopardize polymerization, decrease mechanical strength [14] and create voids that act as water-diffusion pathways across resin-dentin interfaces. The empirical affinity of organic solvents and hydrophilic monomeric moieties for water further contributes to polymer weakening by plasticization after long-term function [9,15]. Ideally, reduced dependency on hydrophilic-based approaches could bridge the gap towards longer resin-dentin interfacial stability.

Curiously, the concept of hydrophobic bonding was proposed almost two decades ago [5]. This bonding approach was effective to reduce the overall hydrophilicity of resin-dentin interfaces. Increasing both the hydrophobic nature of etched dentin and the hydrophilicity of a model hydrophobic dimethacrylate monomer (i.e., bisGMA), through ethanol solvation, made possible the infiltration of solvated hydrophobic monomers into acid-etched dentin [5]. The key was to replace dentin's water content with ethanol before application of hydrophobic monomers diluted in ethanol [5]. In fact, comparable bond strengths to those of a conventionally wet-bonded hydrophilic resins were achieved [5]. This concept was certainly a milestone in adhesive dentistry, demystifying the notion that only hydrophilic-based approaches promoted reliable resin-dentin bonding. However, little has clinically changed in this regard [1]. The proposed saturation of dentin with ethanol (ethanol-wet bonding), albeit quite effective in vitro, is rather technique sensitive under inherently moist clinical conditions [16]. The high bonding complexity required to bond hydrophobic resins to dentin [5] and their questioned clinical efficacy [16] has certainly stagnated the progress of hydrophobic dentin bonding. Moreover, the ultimate urge for simplification of adhesive procedures further prevents the wide acceptance of complex bonding protocols by dentists.

Attempting to circumvent technique-sensitivity issues and reduce the complexity of dry-bonding protocols, new approaches have been proposed to facilitate the removal of residual water from resin-dentin interfaces [17–21]. The use of dimethyl sulfoxide (DMSO) as a pretreatment has been an effective strategy to promote better resin-dentin interactions under dry conditions [17–21]. DMSO breaks water self-association tendencies disrupting residual water layers surrounding collagen [22], substantially improving dentin wettability [19,23]. This especially applies to the wettability kinetics of hydrophobic-rich resins [19]. Remarkably, the wettability of a neat hydrophobic-rich resin on DMSO-treated dry dentin can be comparable to that of a solvated hydrophilic resin on moist dentin during clinically relevant application times [19]. Such recently reported findings [19] invariably opened new possibilities to revisit the current dentin-priming concept where solvated hydrophilic monomers are a necessary means to properly bond hydrophobic monomers to demineralized collagen. Therefore, the primary aim of this study was to investigate whether bonding neat hydrophobic-rich resins to etched dentin, under dry conditions, could be effective in the absence of conventional dentin-priming steps employing solvated hydrophilic monomers. The objectives were to evaluate whether a water-free DMSO pretreatment, tested under different application times, would affect resin-dentin bonding outcomes and hybrid layer quality of resins with different solvent contents and hydrophobicities. The tested null hypotheses were that DMSO-dry bonding would have (*i*) no effect on long-term resin-dentin bonding and hybrid layer quality (*ii*) irrespective of application time or resin composition.

2. Materials and methods

Forty-nine sound third molars were selected for this study under a protocol approved by the Ethical Committee, University of Oulu, Finland (#23–2003). Teeth were extracted from patients as part of dental treatments not related to this study. Molars were stored in 0.5 % Chloramine-T immediately after extraction at 4 °C and used within 3 months.

2.1. Experimental design and dentin bonding procedures

The experimental design was composed of three study factors defined as (*i*) "DMSO pretreatment" at three levels (no treatment, DMSO application for 20 or 60 s), (*ii*) "bonding resin composition" at two levels (solvated hydrophilic-rich + neat hydrophobic-rich or neat hydrophobic-rich resins) and "storage time" at two levels (24 h and 2 years). Experimental groups were bonded under dry conditions according to the DMSO-dry bonding protocol, using 50 % (v/v) ethanolic DMSO solutions [18,19]. The wet-bonding protocol bonded with a solvated hydrophilic-rich + neat hydrophobic-rich resins (conventional three-step etch-and-rinse bonding), without DMSO pretreatments, served as an isolated control group. Molars were mounted in acrylic resin 2 mm below the cement-enamel junction and then sectioned perpendicularly to their long axis under cooling to expose mid-coronal flat dentin surfaces with a diamond saw (Isomet 1000 Precision Saw, Lake Bluff, IL, USA) [24]. Absence of remaining enamel on the dentin surfaces was verified with a stereomicroscope (Leica M60, Leica Microsystems, Wetzlar, Germany) at 40 × magnification. Exposed mid-coronal dentin surfaces were finished with 320-grit silicon carbide paper (Buehler-Met) for 60 s under water-cooling for smear layer standardization. Crown segments (n = 7/group) were randomly allocated into groups according to DMSO pretreatment and bonding resin composition. The dentin pretreatment solution, 50 % DMSO (v/v), was prepared by diluting DMSO (Dimethyl sulfoxide, Sigma-Aldrich, St. Louis, MO, USA) in ethanol (Ethanol 99.8 %, Sigma-Aldrich). Dentin surfaces were etched for 15 s with 32 % phosphoric acid (Scotchbond Universal Etchant, 3 M ESPE, St. Paul, MN, USA), rinsed for 15 s and blot-dried. 50 μL [21] of the DMSO pretreatment solution was actively applied on etched-dentin surfaces for 20 or 60 s and air-dried for 30 s (DMSO-dry bonding) before the application of bonding resins [17–21]. Untreated groups received no DMSO pretreatment and moisture control was performed by air-drying for 30 s (dry bonding). Similarly, the isolated control group received no DMSO treatment, but moisture control was performed by blot-drying, until paper filters presented no visible moisture creating a partially wet surface (conventional etch-and-rinse wet-bonding approach). The inclusion of such isolated control group allowed comparisons of the proposed DMSO-dry bonding protocols to the current gold-standard approach for etch-and-rinse bonding [1,12]. A water-based three-step etch-and-rinse adhesive (Scotchbond Multi-Purpose, 3 M-ESPE) was selected for bonding. Composition of the adhesive system and bonding procedures are shown in Table 1. The *Primer* resin of three-step etch-and-rinse adhesive (Scotchbond Multi-Purpose *Primer*, 3 M-ESPE) was selected as the solvated hydrophilic-rich resin, while the *Bond* resin (Scotchbond Multi-Purpose *Bond*, 3 M-ESPE) was the neat hydrophobic-rich resin. For solvated hydrophilic-rich + neat hydrophobic-rich groups (Primer+Bond), the *Primer* resin was applied for 10 s and gently air-blown for 10 s, followed by the *Bond* resin for 10 s and gently air-blown for 5 s. For the neat hydrophobic-rich groups (*Bond*) the *Bond* resin for 20 s and gently air-blown for 5 s. The total application time was kept constant, 20 s, for both resin applications. The *Primer* and *Bond* resins were both actively applied in a single coat with slight pressure of approximately 4 g [25] in circular rubbing movements. Bonding and restorative procedures were carried out at 23 °C and a relative humidity between 45 – 55 %. Bonding resins 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 Supreme XTE, 3 M ESPE) in two increments of approximately 2 mm. Each increment was light cured for 20 s. Bonding procedures were carried out by a single operator. The restored crown segments were stored in distilled water for 24 h at 37 °C and longitudinally sectioned with a slow-speed diamond saw (Isomet, Buehler Ltd) under water-cooling into resin-dentin beams with cross

Table 1
Materials, composition and application modes. Table 1 – Adhesive System, main components, dentin pretreatments and application modes.

Adhesive system	Components	Pretreatment	Dentin moisture	Bonding agents	Application mode*
Scotchbond Multi-Purpose (3 M/ESPE; SBMP) Batch #	*Primer*: water (>40 %), HEMA, polyalkenoic acid methacrylate copolymer	No treatment	Wet bonding (Isolated control)	Primer+Bond	*a, b, c, f, g, h, i, j*
			Dry bonding	Primer+Bond	*a, b, c, d, e, f, g, h, i, j*
				Bond	*a, b, c, d, e, h, i, j*
		DMSO/EtOH 60 s	Dry bonding	Primer+Bond	*a, b, c, d, e, f, g, h, i, j*
	Bond: bis-GMA, HEMA, dimethacrylates photoinitiators			Bond	*a, b, c, d, e, h, i, j*
		DMSO/EtOH 20 s	Dry bonding	Primer+Bond	*a, b, c, d, e, f, g, h, i, j*
				Bond	*a, b, c, d, e, h, i, j*
Scotchbond Universal Etchant (3M- ESPE)	37 % phosphoric acid, fumared silica (pH 0.6)				*a, b*

Abbreviations: HEMA = 2-hydroxyethyl methacrylate; bis-GMA = bis-phenol diglycidylmethacrylate; * *a*: dentin etching for 15 s; *b*: water rinsing for 15 s; *c*: blot-drying leaving dentin slight moist; *d*: DMSO pretreatment according to the designated application time; *e*: air-drying for 30 s; *f*: active *Primer* active application for 10 s; *g*: gentle blow-drying for 10 s; *h*: active *Bond* application for 10 s; *i*: air-drying for 5 s and *j*: light curing for 10 s

sectional area of approximately 0.8 mm^2. A minimum of 18 resin-dentin beams were sectioned per tooth.

2.2. Resin-dentin beam storage

Resin-dentin beams were randomly selected for the microtensile test and nanoleakage analyses under two conditions: immediate, after 24 h of storage in distilled water, or long-term ageing, after two years in artificial saliva at 37 °C. Half of the beams were randomly used for immediate testing and the other half for long-term ageing. The artificial saliva (pH 7.4) was composed of 5 mM HEPES, 2.5 mM $CaCl_2{\cdot}H_2O$, 0.05 mM $ZnCl_2$ and 0.3 mM NaN_3 at 37 °C [26]. It was changed biweekly to avoid pH changes [24].

2.3. Microtensile bond strength test (μTBS)

Microtensile bond strength testing followed the Academy of Dental Materials guidelines for non-trimmed μTBS testing [24]. A minimum of six resin-dentin beams were tested per tooth (n = 7 teeth/group) after each storage period (24 h and 2 years). Resin-dentin 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 (Shimadzu, AGS-X, Maryland, 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 equation $\mu TBS = P/CA$ was used to calculate bond strength values in MPa. A single blinded operator performed all measurements. Since tooth was considered as the statistical unit, bond strengths of resin-dentin beams from each tooth were averaged [24]. Pre-test failures were considered as 0 MPa for the statistical analysis. A blinded operator performed all measurements. Fractured resin-dentin beams were analyzed with a stereomicroscope (Leica MD60, Leica Microsystems) at 40 × magnification to determine fracture patterns. Unidentifiable surfaces were examined by scanning electron microscopy (SEM) (Phenom ProX, Phenom-World, Eindhoven, Netherlands). Fracture modes were classified as (A) adhesive failure, (C) cohesive failure in composite or dentin and (M) mixed failure (failure at composite/dentin interface with cohesive failure of any substrates) [18].

2.4. Interfacial nanoleakage evaluation (SEM)

Two resin-dentin beams per tooth (n = 7 teeth/group) after each testing period (24 h and 2 years) were randomly selected to evaluate silver nitrate uptake at bonded interfaces. Nanoleakage evaluation was performed according to a protocol previously described by Tay *et al.* [27]. Resin-dentin beams were initially wet polished with 600-grit SiC paper and coated with two layers of nail varnish applied up to 1 mm of the bonded interfaces. Coated samples were rehydrated in distilled water for 1 h and immersed in 50 % (w/v) ammoniacal silver nitrate (pH 9.5) for 24 h. After thorough rinsing in distilled water for 120 s, samples were immersed in photo-developing solution (Kodak Professional D-76 developer, Kodak Rochester, NY, USA) for 8 h under fluorescent light. Silver impregnated resin-dentin beams were embedded in epoxy resin, wet polished with 600-, 1200-, 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 then ultrasonically cleaned in distilled water for 120 s, air-dried for 2 h, mounted on aluminum stubs, dried in silica overnight and carbon sputtered. Nanoleakage was qualitatively analyzed using a scanning electron microscope (Phenom ProX, Phenom-World) on backscattering mode at 10 kV. Silver uptake patterns and extensions were evaluated by a blinded operator at magnifications ranging from 1000 − 10000 × .

2.5. Hybrid layer characterization (SEM)

Two resin-dentin beams from each tooth were randomly selected for hybrid layer characterization under SEM. Resin-dentin beams were embedded in epoxy resin and wet-polished with 600-, 1200-, 2000- and 1, 0.25 (MetaDi, Buehler Ltd) and 0.05 μm (MasterPrep, Buehler Ltd) polishing pastes. Samples were then ultrasonically cleaned in distilled water for 120 s. Bonded interfaces were then treated with 50 % H_3PO_4 for 5 s and 3 % NaOCl for 10 min followed by dehydration in ascending ethanol series (50, 70, 80, 90 and 3 × 100 %), fixed in hexamethyldisilazane, sputtered with gold/palladium and analyzed on backscattering mode at 10 kV (Phenom ProX, Phenom-World). A series of sequential micrographs of the entire bonded interfaces (5000 × magnification) were obtained from each resin-dentin beam. Three randomly selected areas on each micrograph, located between adjacent resin tags, were analyzed and hybrid layer thickness were measured using an open-source image software (ImageJ, National Institute of Health, Bethesda, MD, USA). Measurements were averaged to determine the mean hybrid layer thickness for each tooth (n = 7).

2.6. Statistical analysis

Bond strength data (Kolmogorov-Smirnov, $p = 0.067$; Brown-Forsythe Test, $p = 0.923$) was analyzed by three-way ANOVA followed by the Tukey test. Dunnett's test compared the conventional wet-boding technique (Primer+Bond), isolated control group, to the remaining experimental groups. Hybrid layer thickness data (Shapiro-Wilk, $p = 0.32$; Brown-Forsythe Test, $p = 0.38$) was analyzed by two-way ANOVA followed by the Tukey test. Statistical significance was set at $\alpha = 0.05$. Calculations were performed by SigmaPlot for Windows, version 14.0 (Alfasoft AB, Sweden).

3. Results

3.1. Microtensile bond strength

The cross-sectional area of resin-dentin beams (0.79 mm^2 ± 0.07) ranged from 0.62 to 0.89 mm^2 without significant differences regarding specimen size between groups ($p = 0.097$). Three-way ANOVA revealed that "DMSO pretreatment" ($p < 0.001$; $\eta2 = 0.88$), "bonding resin composition" ($p < 0.001$; $\eta2 = 0.67$), "storage time" ($p < 0.001$; $\eta2 = 0.40$) and the interactions between "DMSO pretreatment" * "bonding resin composition" ($p = 0.001$; $\eta2 = 0.22$) and "DMSO pretreatment" * "bonding resin composition" * "storage time" ($p = 0.007$; $\eta2 = 0.13$) had significant effects on resin-dentin bond strengths. Bond strength means and standard deviations are reported in Fig. 1. Untreated dry dentin produced the lowest bond strengths, roughly 80 % lower compared to the isolated control group (conventional wet bonding) ($p < 0.05$). Resin composition affected immediate bond strengths of untreated dentin. Untreated dry dentin bonded with the neat hydrophobic-rich resin (Bond) produced significantly lower bond strengths than solvated hydrophilic-rich + neat hydrophobic-rich (Primer+Bond) ($p < 0.05$).

DMSO pretreatments produced significantly higher bond strengths (up to 6-fold) compared to untreated dentin regardless of resin composition, time of application or storage time ($p < 0.05$). Primer+Bond bonding combinations produced bond strengths roughly 40 % higher than protocols employing only the neat hydrophobic-rich resin (Bond) regardless of DMSO-pretreatment application time ($p < 0.05$). Pretreatment application for 60 s produced significantly higher bond strengths compared to 20 s considering bonding protocols with similar resin combinations ($p < 0.05$). In general, immediate bond strengths of DMSO-pretreated dentin under dry conditions were comparable or significantly higher ($p < 0.05$) than the conventional wet-bonding approach (Control). The only exception occurred for the neat hydrophobic-rich resin (Bond) combined with the 20 s DMSO pretreatment, which showed significantly lower bond strengths ($p < 0.05$).

Long-term ageing had deleterious effects on bond strengths depending on the bonding protocols. Conventional wet-bonding (Control) produced significantly lower values after ageing (roughly 50 % lower), similarly to untreated dry groups for both Primer+Bond (60 % lower) and *Bond* (70 % lower) resins ($p < 0.05$). Ageing had no significant effects on bond strengths of Primer+Bond DMSO-dry groups, regardless of application time, ($p > 0.05$) which produced significantly higher bond strengths than the conventional wet bonding (Control) ($p < 0.05$). DMSO-dry groups bonded with the neat hydrophobic-rich resin (Bond) presented significantly lower bond strengths after ageing ($p < 0.05$), albeit values were not statistically different from the conventional wet-bonding (Control) ($p > 0.05$). Fracture pattern distributions (%) for all groups are shown in Fig. 2. Table 2 shows the number of fractured resin-dentin beams. The predominant failure mode at 24 h was mixed for all groups, except for untreated samples bonded with the neat hydrophobic-rich resin (Bond) showing a higher number of adhesive failures. After ageing, untreated groups showed a considerable increase in adhesive failures, with a higher number of pre-test failures for dry-bonded groups. DMSO-dry groups showed a slight increase in adhesive failures after ageing, except for the neat hydrophobic-rich resin (Bond) DMSO-pretreated for 20 s

3.2. Interfacial nanoleakage evaluation (SEM)

Representative SEM micrographs of silver infiltration across hybrid layers are shown in Fig. 3. Silver deposits were identified in hybrid layers and/or surrounding areas of all resin-dentin beams. At 24 h, untreated dry-bonded samples presented the highest levels of silver uptake at hybrid layers. Bonding dry-untreated dentin with the neat hydrophobic-rich resin (Bond) produced heavy reticular silver deposits across hybrid layers. Bonding the solvated hydrophilic-rich + neat hydrophobic-rich resins (Primer+Bond) to untreated dry dentin also presented substantial reticular silver deposits across hybrid layers, but to a lesser extent than samples bonded with neat hydrophobic-rich resin (Bond). Such high levels of silver uptake depicted large extensions of water-filled porous zones for dry-untreated dentin, regardless of the bonding resins. DMSO pretreatments for 60 or 20 s (DMSO-dry 60 s or DMSO-dry 20 s) considerably reduced silver impregnation within hybrid layers for both bonding resins. Both application times produced comparable silver uptake for Primer+Bond, resulting in lower nanoleakage than the conventional wet bonding (Control). Nanoleakage patterns were predominantly characterized as spotted silver deposits lightly distributed along hybrid layers for both application times. DMSO-dry 60 s produced higher silver uptake than conventional wet bonding (Control) when the neat hydrophobic-rich resin (Bond) was used. Nanoleakage patterns were mostly seen as spotted silver deposits distributed across the hybrid layer; while for the conventional wet bonding (Control), silver deposits were predominantly identified as

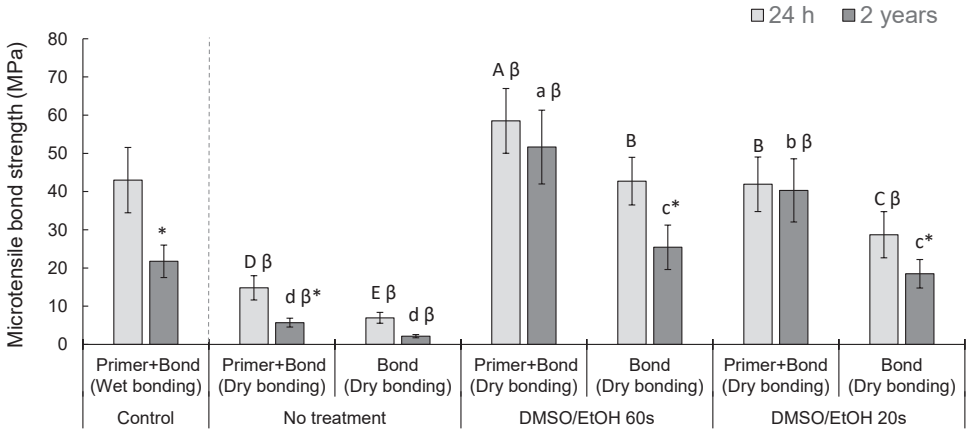

Fig. 1. Microtensile bond strength (MPa) means and standard deviations of solvated hydrophilic-rich + neat hydrophobic-rich (Primer+Bond) or neat hydrophobic-rich resins (Bond) of a commercial three-step etch-and-rinse adhesive (Scotchbond Multi-purpose, 3MESPE) bonded to DMSO-treated dentin (50 % DMSO ethanolic solutions v/v) with different application times (60 or 20 s) under dry conditions. The conventional wet-bonding technique (Primer+Bond) served as an isolated control group. Resin-dentin beams were tested at 24 h or after two-year ageing in artificial saliva at 37 °C. Tooth was considered the statistical unit (n = 7/group). Different upper-case letters indicate significant differences between dry-bonded groups at 24 h. Different lower-case letters indicate significant differences between dry-bonded groups at 2 years. * indicates significant differences between storage periods within bonded protocols. Statistical comparisons were performed by the Tukey test ($\alpha = 0.05$). β indicates significant differences between the isolated control group and dry-bonding protocols within storage periods according to the Dunnett's test ($p < 0.05$).

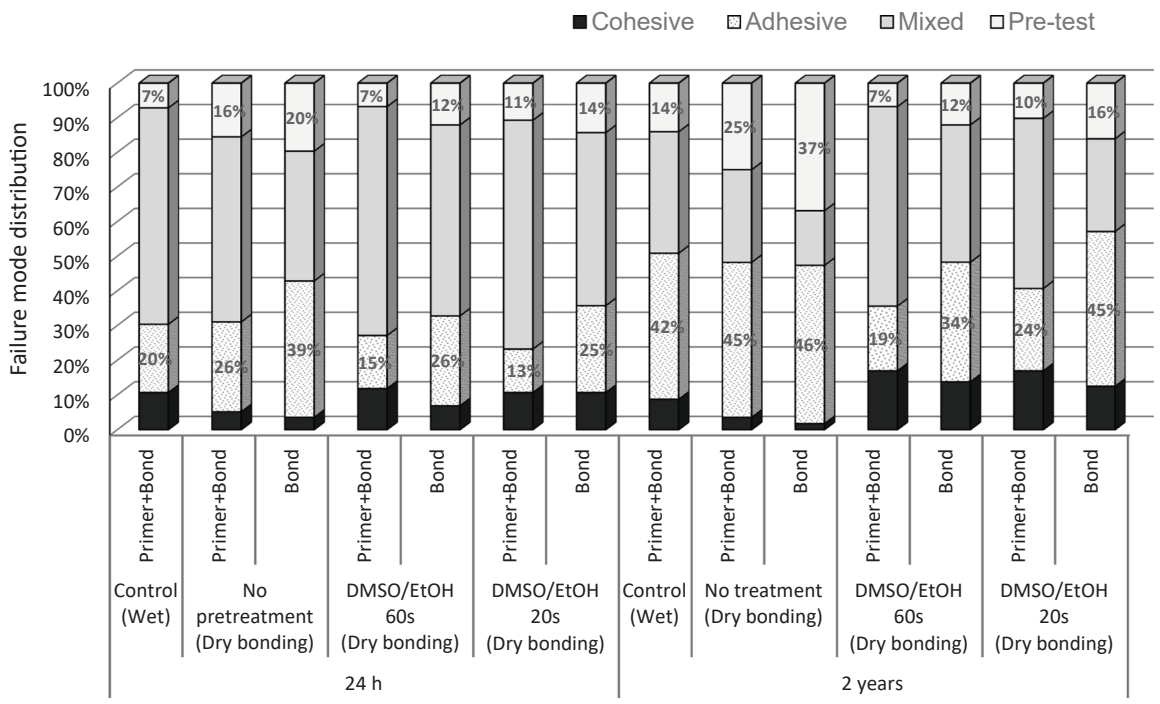

Fig. 2. Fracture patterns in percentages (%) of resin-dentin beams at 24 h and 2 years. Fracture patterns were classified as: cohesive failure = failure exclusive within dentin or resin composite; adhesive failure = failure at resin/dentin interface and mixed failure = failure at resin/dentin interface with cohesive failure of the neighboring substrates.

Table 2
Microtensile bond strength means (MPa), standard deviations (± SD) and number of specimens according to fracture mode.

	Control	No treatment		DMSO/EtOH 60 s		DMSO/EtOH 20 s	
	Primer+Bond (Wet bonding)	Primer+Bond (Dry bonding)	Bond (Dry bonding)	Primer+Bond (Dry bonding)	Bond (Dry bonding)	Primer+Bond (Dry bonding)	Bond (Dry bonding)
24 h	43.01 ± 8.55 [6/11/35/4/56]	14.81 ± 3.18 [3/15/31/9/58]	6.96 ± 1.42 [2/22/21/11/56]	58.50 ± 8.48 [7/9/39/4/58]	42.73 ± 5.81 [4/15/32/7/58]	41.91 ± 7.14 [6/7/37/6/56]	28.71 ± 6.04 [6/14/28/8/56]
2 years	21.75 ± 4.24 [5/24/20/8/57]	5.70 ± 1.16 [2/25/15/14/56]	2.16 ± 0.42 [1/22/13/21/57]	51.65 ± 9.66 [10/11/34/4/59]	25.42 ± 5.81 [8/20/23/7/58]	40.31 ± 8.27 [10/14/29/6/59]	18.49 ± 3.73 [7/25/15/9/56]

Tooth was considered the statistical unit (n = 7/group). Numbers between square brackets represent the number of specimens (resin-dentin beams) 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.

localized reticular agglomerations located at the bottom of hybrid layers. DMSO-dry 20 s bonded with the neat hydrophobic-rich resin (Bond) produced the highest levels of silver uptake. Nanoleakage patterns were characterized as spotted silver deposits containing localized areas of reticular agglomerations throughout most of the hybrid layer thickness.

After ageing, higher nanoleakage levels were identified for all groups: Untreated Dry Bond > Untreated Dry Primer+Bond > DMSO-dry 20 s Bond > DMSO-dry 60 s Bond > Untreated Wet Primer+Bond (Control) > DMSO-dry 20 s Primer+Bond > DMSO-dry 60 s Primer-+Bond. Nanoleakage patterns of untreated dentin consisted mostly of reticular patterns extending across the entire extension of hybrid layers irrespective regardless of bonding resin. DMSO-pretreated samples maintained mostly spotted silver deposits across hybrid layers when the solvated hydrophilic-rich + neat hydrophobic-rich (Primer+Bond) irrespective of application times (20 or 60 s). For the neat hydrophobic-rich resin (Bond), while DMSO-dry 60 s presented mostly spotted silver deposits with some localized reticular depositions at the bottom of hybrid layers, DMSO-dry 20 s showed large occurrences of reticular depositions across hybrid layers.

3.3. Hybrid layer characterization (SEM)

Representative SEM micrographs of hybrid layers are shown in Fig. 4. Hybrid layer thickness ranged from 0.78 to 3.97 μm. Table 3 shows hybrid layer thickness means (μm) and standard deviations for all groups. Two-way ANOVA revealed that “bonding resin composition” ($p < 0.001$; $\eta 2 = 0.63$), “DMSO pretreatment” ($p < 0.001$; $\eta 2 = 0.91$) and their interaction ($p < 0.001$; $\eta 2 = 0.46$) had significant effects on hybrid layer formation. Dry bonding untreated dentin significantly reduced (50 - 70 %) hybrid layer thickness compared to wet bonding ($p < 0.05$). A substantial reduction in resin tag diameter and extension occurred for dry bonding untreated dentin with the neat hydrophobic-rich resin (Bond), resulting in hybrid layers with lesser thickness ($p < 0.05$). For Prime+Bond, DMSO-dry bonding produced significantly thicker hybrid layers than dry bonding ($p < 0.05$), regardless of application time (60 or 20 s). No significant differences were observed between resins for 60 s DMSO-dry bonding ($p > 0.05$) and hybrid layer thickness was comparable to wet-bonding ($p > 0.05$). For the neat hydrophobic-rich resin (Bond), the effect of DMSO-dry bonding on hybrid layer formation was time dependent. Shorter DMSO application times (20 s) significantly reduced hybrid layer thickness (roughly 50 %)

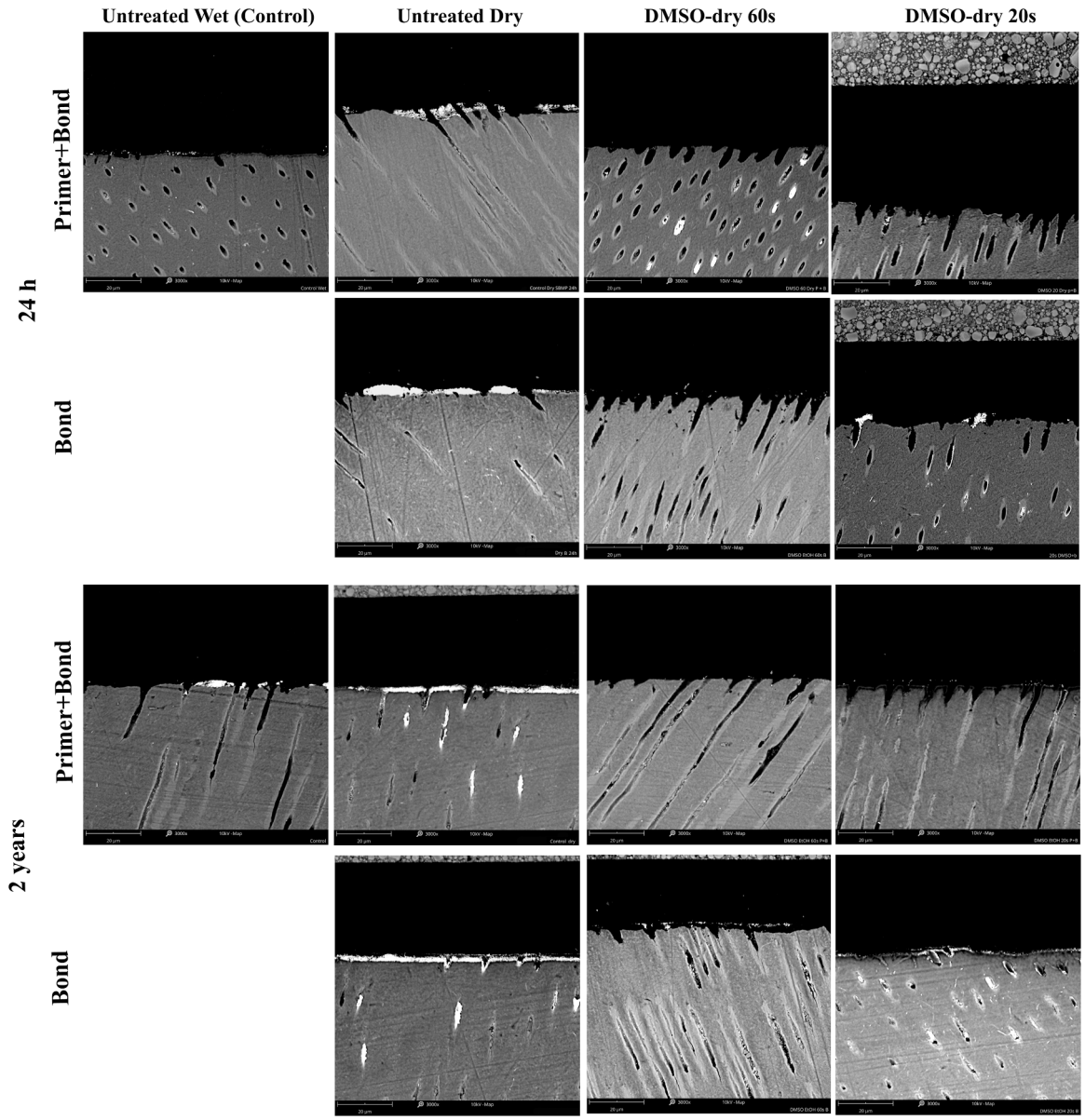

Fig. 3. Representative SEM micrographs showing nanoleakage extensions of solvated hydrophilic-rich + neat hydrophobic-rich (Primer+Bond) or neat hydrophobic-rich resins (Bond) of a commercial three-step etch-and-rinse adhesive (Scotchbond Multi-purpose, 3MESPE) bonded to DMSO-treated dentin (50 % DMSO ethanolic solutions v/v) with different application times (60 or 20 s) under dry conditions. Nanoleakage analysis was performed at 24 h or after two-year ageing in artificial saliva at 37 ℃.

of hydrophobic-rich resins ($p < 0.05$).

4. Discussion

Since the proposed DMSO-dry bonding protocol enabled direct coupling of a neat hydrophobic-rich resin to collagen, the first null hypothesis was rejected. Bonding methacrylate-based monomers to dry collagen, however, is a rather challenging procedure [12,28]. As such, etch-and-rinse adhesives are still preferably bonded to moist dentin [12,28]. Both simplified and multi-step adhesives must properly "prime" dentin to promote good interfacial contact and thus durable-strong interactions [1,12]. Hence, dental adhesives heavily rely on solvated hydrophilic components (monomers and/or solvents) to achieve acceptable resin-dentin bonding [1,13]. In this study, the underperformance of conventional dry bonding (without DMSO pretreatment) occurred regardless of resin composition. It became more evident after long-term ageing, denoting dry bonding's low applicability for routine use. There is a consistent body of evidence showing that air-drying etched dentin forms a near-impermeable membrane-like structure that prevents the permeation of most solvated adhesive monomers [12,28]. This was observed in hybrid layers of untreated dentin produced by the solvated hydrophilic-rich + neat hydrophobic-rich resins (Primer-+Bond) and more notably for the neat hydrophobic-rich resin (Bond). "Priming" air-dried dentin with the water-based hydrophilic resin re-expanded collapsed collagen to some extent [28], but still generated a highly porous interface that yielded low bond strengths (15 MPa). Substantial reductions in bond strengths after ageing (roughly 70 %) clearly indicate that relying solely on the water-content of monomeric primers is insufficient to produce long-term favorable outcomes for extensively air-dried dentin. Previous reports have corroborated the latter [19,25,29]. Unsurprisingly, omitting the water-based priming step (*Primer*) resulted in even lower bond strengths (6 MPa), which would not realistically resist shrinkage stresses inside cavities during light-curing [30].

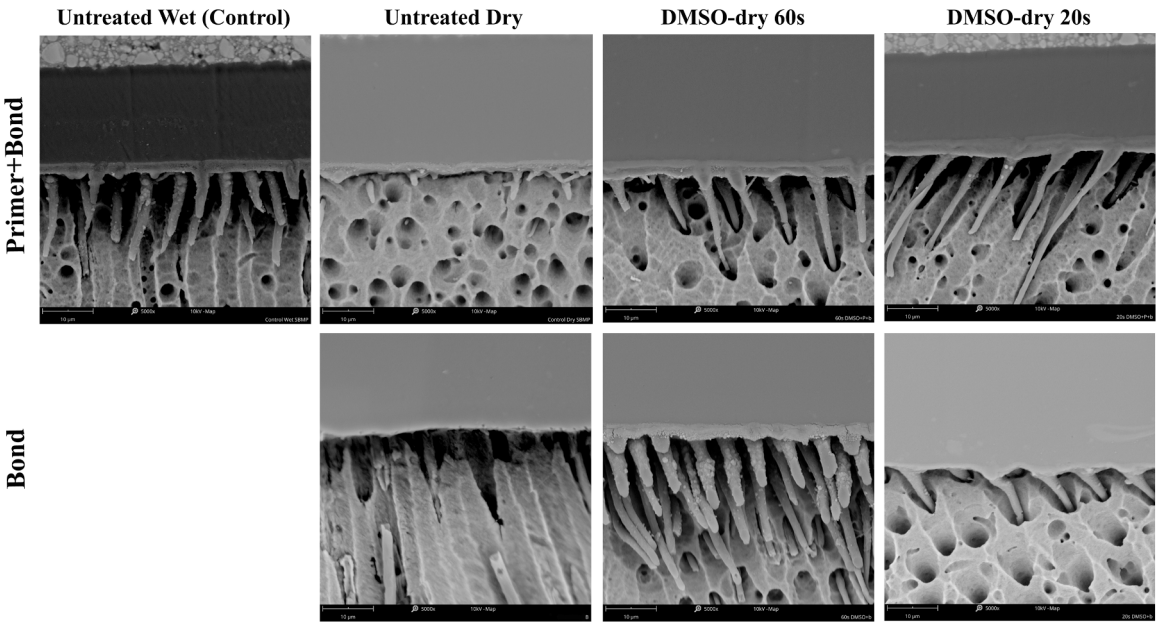

Fig. 4. Representative SEM micrographs showing hybrid layers of solvated hydrophilic-rich + neat hydrophobic-rich (Primer+Bond) or neat hydrophobic-rich resins (Bond) of a commercial three-step etch-and-rinse adhesive (Scotchbond Multi-purpose, 3MESPE) bonded to DMSO-treated dentin (50 % DMSO ethanolic solutions v/v) with different application times (60 or 20 s) under dry conditions.

Table 3
Hybrid layer thickness (μm) and standard deviations.

	No pretreatment (Wet bonding)	No pretreatment (Dry bonding)	DMSO/EtOH 60 s (Dry bonding)	DMSO/EtOH 20 s (Dry bonding)
Primer+Bond	3.25 ± 0.37	$1.2^{Ba\ \beta}$ ± 0.14	3.37^{Aa} ± 0.36	3.00^{Aa} ± 0.44
Bond	-	$0.83^{Cb\ \beta}$ ± 0.12	3.04^{Aa} ± 0.41	$1.53^{Bb\ \beta}$ ± 0.24

Different upper-case letters indicate significant differences between dentin pretreatments (rows). Different lower-case letters indicate significant differences between adhesives (columns). Statistical comparisons were performed by the Tukey test ($\alpha = 0.05$). β indicates significant differences between the isolated control group No pretreatment (Wet bonding) and dry-bonding protocols according to the Dunnett's test ($p < 0.05$).

Clearly, the attempt to directly bond neat hydrophobic-rich resins to dry-etched dentin is undoubtedly an inefficient bonding approach fated to failure when following established bonding protocols [1,12]. Differences in the solubility parameters [5] between commonly used dimethacrylates (i.e., bisGMA, UDMA, 10-MDP) and the inherently moist etched dentin [2] hinder collagen perfusion by relatively hydrophobic monomers [12,31]. Resin blends undergo phase changes [11], forming resin globules that remain suspended in water instead of polymerizing into a protective-solid network [32]. In this study, the tested hydrophobic-rich resin (Bond) was incapable to directly interact with dentin and replace the water content surrounding exposed collagen. Highly porous weakly bonded interfaces were formed already at 24 h and more profoundly after long-term storage. The strictly limited hybrid layer thickness (< 1 μm) highlighted the inability of relatively hydrophobic monomers to infiltrate demineralized collagen. Moreover, the substantial increase in the number of pre-test failures after ageing reiterates the bonding incompatibility between neat hydrophobic-rich resins directly applied to collagen. Even though collagen dehydration further interferes with efforts to bond methacrylate-based resins to etched dentin [19,25,28,29], it was a cornerstone here to bond neat hydrophobic-rich resins to etched dentin for the first time.

Lowering dentin's water-content helped increase the hydrophobic nature of collagen [33] to more closely match that of the hydrophobic-rich bonding resin. The challenge was to air-dry collagen, while preserving sufficient interfibrillar spaces for proper resin infiltration. As such, the DMSO-dry bonding approach was selected due to its unique ability to improve resin-dentin bonding by modifying interactions among collagen, water and resin components [19]. Similarly to other polar organic solvents (i.e. acetone, ethanol, propanol and methanol) [34,35], DMSO also stiffens demineralized collagen [18]. The tested water-free pretreatment (50 % DMSO/EtOH v/v) can increase the elastic modulus of collagen by 12.1-fold, conferring higher dimensional stability without substantial compromise of interfibrillar spaces [18]. Comprehensibly, DMSO-induced collagen stiffening also implies in further reduction in water-content [36], raising concerns about collagen shrinkage before hybridization due to higher interpeptide hydrogen bonding [28]. However, previous findings have shown that interfibrillar spaces may be sufficiently maintained for proper resin infiltration under dry conditions [18,19]. Comparable hybrid layer thickness of DMSO-dry bonded (for 60 s) hydrophobic-rich resin (roughly 3.04 μm) and the conventional wet-bonding approach (3.25 μm) indirectly suggests potential similarities in resin infiltration. Noteworthy, bonding outcomes depended on DMSO application times. While DMSO-dry bonding for 20 s improved bond strengths of the tested hydrophobic-rich resin, hybrid layer quality was inferior. Longer DMSO application times resulted in better resin infiltration (i.e., thicker hybrid layers with lower porosities) and higher bond strengths. Thus, the second null hypothesis was rejected. DMSO-dry bonding for 60 s clearly modified the bonding behavior of the tested hydrophobic-rich resin. Bond strengths were comparable to conventional "gold standard" wet-bonding protocols immediately and after long-term ageing. Determining which exact mechanism of DMSO-dry bonding had the biggest impact on direct coupling the neat hydrophobic-rich resin to dentin is beyond the scope of this study. It is plausible to assume that in addition to elevating dentin's hydrophobic nature via air-drying [33], DMSO's modification of the wetting behavior [19,23] was critical to allow resin-dentin bonding under such extreme conditions.

Wetting is a primary requirement to achieve good bonding [1]. For clinically relevant application times, the wettability of DMSO-pretreated dry dentin by a neat hydrophobic-rich resin is comparable to that of moist dentin receiving a solvated hydrophilic resin [19]. Better

wettability allowed a more intimate contact between the neat hydrophobic-rich resin and DMSO-pretreated dentin (for 60 s), improving hybrid layer formation and adhesion. DMSO breaks water's self-associative tendency disrupting and rearranging water molecules [37] that surround collagen [22]. The oxygen molecule in DMSO hydrogen bonds with two water molecules while the methyl groups (-CH_3) in DMSO forming hydrophobic ends [22]. This exposes diffusion sites facilitating the interaction of hydrophobic monomers with collagen. The results of this study provide the proof of concept that bonding neat hydrophobic-rich resins to collagen is indeed possible without a separate priming-step containing solvated hydrophilic monomers. It is prudent to point out that the proposed bonding protocol should be further optimized to improve the long-term integrity of hybrid layers. The absence of an adjunctive diluent in resin blends approximate monomers and reduce their mobility. The relatively strong intermolecular hydrogen-bonding interactions between hydroxyl (OH) and carbonyl groups (C═O) in distinct bis-GMA monomers [38] increases viscosity, which can retard/diminish monomer infiltration. Infiltration dynamics is controlled by capillary and viscous flows. Adhesive spreading and infiltration occurs simultaneously, but not necessarily at the same relative rate due to differences in resin viscosity. This may explain the differences in hybrid layer integrity between wet-bonding and the neat hydrophobic-rich resin bonded to DMSO-pretreated dentin (60 s), in spite of their comparable wettability [19]. It is plausible to speculate that prolonged application times may be necessary [39] for neat hydrophobic resins to permeate collagen due to their higher viscosity. Future studies should explore different compositions of hydrophobic-rich resin blends to optimize both DMSO and resins' application times.

Considering that resin-dentin interfaces may endure clinical service times for over 30 years [40], polymer networks inside hybrid layers should be insoluble materials with high long-term stability. Water entrapment within hybrid layers during light-curing precludes the formation of highly cross-linked polymeric networks, making the adhesive interface more prone to failure over time [1,7]. Strength reductions of hybrid layer after water storage can be attributed to their hydrophilic characteristics [10]. Additonally, the higher the solvent content in bonding resins before light-curing, the lower the conversion degree and the mechanical properties of the formed polymer [41]. Hence, the rationale for designing a protocol that allowed bonding neat hydrophobic-rich resins under dry conditions was to delay or possibly prevent hydrolytic degradation to ultimately extend the durability of bonded interfaces [1,5,6]. Even though direct bonding of neat hydrophobic-rich resins produced comparable long-term bonding outcomes to "gold standard" wet-bonding protocols, conventional "priming" of DMSO-treated dentin with water-based hydrophilic resin [42] still presented the best long-term outcomes. DMSO's potential to extend the longevity of resin-dentin bonds [22,43,44] was somewhat limited by the stronger intermolecular interactions of the more viscous neat resin. This extreme bonding condition should be viewed as a proof of concept for reducing the dependency on solvent content to bond hydrophobic-rich resins to dentin. Nonetheless, this study provides evidence that shorter DMSO-application times (20 s) may be viable to also improve bond strengths and reduce long-term hybrid layer degradation when dry dentin is conventionally "primed" with a water-based hydrophilic resin. This could simplify DMSO-dry bonding protocols for future applications contributing to shorter executions and possibly better receptivity by clinicians.

5. Conclusions

Neat hydrophobic-rich resins may be directly coupled to acid-etched dentin by lowering dentin's hydration state before hybridization. This highlights the applicability of the DMSO-dry bonding approach to create resin-dentin interfaces with higher hydrophobicity without the mandatory use of solvated resins containing hydrophilic monomers. Direct bonding of neat hydrophobic-rich resins to air-dried dentin can indeed match those of established "gold standard" wet-bonding protocols. Nonetheless, the conventional use of solvated hydrophilic resins with longer DMSO-application times may still result in better bonding outcomes. Reduced dependency on solvated hydrophilic monomers for dentin priming may shine some light into new bonding strategies to ultimately extend the durability of resin-dentin interfaces. This proof of concept should be further optimized before clinical application.

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