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Nanofiller Particles and Bonding Durability, Water Sorption, and Solubility of Universal Adhesives

VG Araújo-Neto • MM Moreira • R Ñaupari-Villasante
DM De Paula • STCB Medeiros • AD Loguercio • VP Feitosa

Clinical Relevance statement

The commercial universal adhesive containing silanized nanofiller particles decreased dentin bond durability and increased water sorption, which could be reversed by using unfilled adhesive.

SUMMARY

The aim of this study was to evaluate the influence of nanofiller particles in simplified universal adhesive on the long-term microtensile bond strength and silver nitrate uptake, as well as water sorption and solubility. Commercial adhesives Ambar Universal (FGM) in nanofilled-containing version (filled) and same lot without fillers (unfilled) were donated and applied by means of etch-and-rinse strategy. Microtensile bond strength was surveyed after 24-hours or 1-year water storage. Silver nitrate uptake was assayed using scanning electron microscopy (SEM). Water sorption and solubility experiments were performed based on ISO 4049:2009. Statistical analysis was performed using two-way ANOVA and Tukey test ($p<0.05$). The bond strength of both the adhesives were statistically similar at 24 hours ($p>0.05$), but the filled group attained significant bond strength reduction after aging when compared to initial bond strength ($p<0.001$). Conversely, unfilled adhesive presented stable adhesion after 1-year storage ($p=0.262$). Silver nitrate uptake was similar for both adhesives, with little silver impregnation at the hybrid and adhesive layers. Water sorption was higher with filled adhesive compared to the unfilled one ($p=0.01$). Conversely, solubility was higher in unfilled in comparison to filled one ($p=0.008$). The presence of nano-

*Vitaliano Gomes Araújo-Neto, Department of Restorative Dentistry, Piracicaba Dental School, University of Campinas, Piracicaba, SP, Brazil

Madiana Magalhães Moreira, DDS, MS, Post-graduation Program in Dentistry, Federal University of Ceará, Fortaleza, Brazil

Romina Ñaupari-Villasante, DDS, Department of Restorative Dentistry, State University of Ponta Grossa, Ponta Grossa, Brazil

Diego Martins De Paula, DDS, MS, PhD, Paulo Picanço School of Dentistry, Fortaleza, Brazil

Samara Tabata Cavalcante Braga Medeiros, DDS student, Paulo Picanço School of Dentistry, Fortaleza, Brazil

Alessandro Dourado Loguercio, DDS, MS, PhD, Department of Restorative Dentistry, State University of Ponta Grossa, Ponta Grossa, Brazil

Victor Pinheiro Feitosa, DDS, MS, PhD, Paulo Picanço School of Dentistry, Fortaleza, Brazil

*Corresponding author: 901 Av Limeira, Areião, Piracicaba, São Paulo, Brazil, zip code: 13414-903; e-mail: vitalianoganeto@gmail.com

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fillers in universal adhesive achieves higher water sorption and dentin bond degradation, which did not occur in the unfilled adhesive.

INTRODUCTION

Chewing stresses in the oral environment clinically challenge the bonding interface between resin composite and adhesive. Although dental adhesives have satisfactory initial bonding to dental substrates, these materials may fail after relatively short-term aging periods.[1,2] Among etch-and-rinse and self-etch adhesives, the etch-and-rinse bonding mechanism relies on micromechanical retention triggered by phosphoric acid etching's superficial dissolution of enamel or dentin.[3] In the self-etch approach, the chemical bond of functional monomers with calcium and hydroxyapatite plays a further role in dentin/enamel bonding along with micromechanical interlocking. Furthermore, simplified self-etch adhesives evolved to modern multimode universal adhesives, which may be applied in both bonding strategies.[4,5]

The acid etching procedure requires effective dentin humidity control to result in optimal penetration of monomers into the interfibrillar spaces of the collagen matrix,[3] in order to diminish hydrolytic degradation. However, most hydrophilic monomers are mono-methacrylates, thereby presenting linear polymer chains being more prone to leaching and hydrolysis.[6-8]

Although, not all simplified adhesive systems contain nanofiller particles, by analogy with restorative resin composites, the addition of nanofillers increases the mechanical properties of the adhesive material itself.[9,10] However, when the immediate bond strength to dentin was evaluated, controversial results were observed.[11,12] Actually, the addition of these particles increases the material viscosity while decreasing the polymerization stresses and shrinkage when compared to unfilled adhesives.[13]

One concern is related to the coating of these nanofillers with relatively hydrophilic silane to bond the polymer chains to the fillers. Such silane coating has lower resistance to hydrolysis and may cause the detachment of fillers after aging *in vitro*, which was even found *in vivo*.[1,2,6]

However, a recent systematic review of clinical trials showed that no significant improvement in terms of clinical performance of the adhesive restoration in noncarious cervical lesions when micro-/nanofilled and unfilled adhesives were compared.[14] Indeed, there are contradictory outcomes and lack of resin–dentin long-term water storage evaluation on this issue. Particularly, an adequate study could highlight the actual influence of fillers on water uptake and dentin bond durability, when the same composition of simplified universal adhesive with or without nanofiller particles is evaluated.

Therefore, the aim of this study was to survey the influence of nanofillers on the same universal adhesive, ie, nanofilled-containing (filled) and unfilled (unfilled), after 24 hours or 1 year of water storage. The null hypothesis was that the presence/absence of nanofillers will not interfere with dentin bond strength and silver nitrate uptake, as well as with water sorption and solubility of the adhesive material.

METHODS AND MATERIALS

Sample Preparation

The Ambar Universal adhesive (FGM, Joinville, Brazil) was provided by the manufacturer in a nanofiller-containing commercial version (filled, batch number 040218) and the same lot without nanofiller particles (unfilled). Both adhesives were applied and light cured in the same manner, for standardization purposes. Three laboratory experiments were performed: microtensile bond strength after 24-hours or 1-year water storage, silver nitrate uptake, water sorption, and solubility.

Microtensile Bond Strength Testing (μTBS)

Twenty extracted third molars were divided into two groups (n=10). The teeth were stored in 0.5% thymol/water solution at 4°C for no longer than 4 months. They were cut to expose mid-coronal flat dentin surfaces and to remove the roots by means of a diamond saw in a metallographic cutting machine (Isomet 1000, Buehler, Lake Blufff, IL, USA). Dentin surfaces were polished with 320-grit SiC abrasive papers under running water for 30 seconds to create standardized smear layers. All teeth were bonded following etch-and-rinse strategy. They were etched for 15 seconds with 37% ortho-phosphoric acid (Condac 37, FGM), washed vigorously for 30 seconds with distilled water, and dentin was kept visually moist by using blot-wet cotton pellets. Teeth were randomly assigned to one of the two adhesives (filled or unfilled), and the adhesive was actively applied in two coats—rubbing each coat for 20 seconds with a gentle air blast between the coats. Following, the adhesive was light cured for 40 seconds with a DB-685 LED unit (1200 mW/cm^2, Dabi Atlante, Rio de Janeiro, Brazil). After adhesive curing, five 1-mm-thick increments of resin composite (Opallis, FGM)

were applied horizontally and individually light cured for 40 seconds each. Resin-bonded teeth were sectioned in resin–dentin-bonded sticks (0.9±0.2 mm^2 cross-sectional area) suitable for microtensile bond strength testing. Sticks were stored immersed in distilled water for 24 hours or 1 year (with monthly water exchange) prior to testing. Afterwards, resin–dentin-bonded sticks were glued to Geraldelli jigs with cyanoacrylate gel (Super Bonder gel; Loctite Henkel, Rocky Hill, USA) and tested in a universal testing machine (DL 2000, EMIC, São José dos Pinhais, PR Brazil) with a 500-N load cell at 0.5 mm/minute crosshead speed. Subsequent to the μTBS testing, the failure mode of each fractured stick was determined using a stereomicroscope with 100× magnification (Olympus Sz 40–50, Tokyo, Japan). The fractures were classified as adhesive, mixed, cohesive in composite or cohesive in dentin. After passing normality and homoscedasticity tests (data not shown), the μTBS data were statistically analyzed using two-way ANOVA (presence of fillers and aging period) and Tukey test at $\alpha = 0.05$.

Silver Nitrate Uptake Evaluation

Two resin–dentin-bonded sticks from the central region of each bonded tooth were selected from each subgroup (n=20) and processed for silver nitrate uptake assessment, as previously described.[15] In brief, resin–dentin–bonded sticks were immersed in 50 wt% ammoniacal silver nitrate [Ag(NH_3)2]NO_3(aq) solution in total darkness for 24 hours. Subsequently, the specimens were rinsed with distilled water to remove excess silver nitrate and then immersed in a photo-developing solution for 8 hours under fluorescent light (60 cm from the specimens) to reduce silver ions into metallic silver grains along the resin–dentin interface. The silver-impregnated sticks were embedded in epoxy resin and wet polished using #600, #1200, #2000 SiC papers and diamond pastes 3, 1, and 0.25 μm (Buehler) in polishing cloths. The specimens were ultrasonically cleaned for 20 minutes after each abrasive/polishing step. Finally, they were air dried, dehydrated for 48 hours, coated with carbon and observed using scanning electron microscopy (SEM) (Inspect 50, FEI, Amsterdam, Netherlands) in backscattered electron mode to evaluate silver impregnation.

Water Sorption and Solubility

The water sorption and solubility experiments were performed based on ISO 4049:2009 protocol.[16] Ten disk-shaped specimens (6.0±0.1-mm diameter × 1.0±0.1-mm thickness) were prepared for each material (n=10). The specimens were created in standardized silicone molds and were individually light cured using a DB685 LED unit (Dabi Atlante) with 1200 mW/cm^2 irradiance for 40 seconds. After 24-hour storage in darkness, the specimens were placed in a desiccator containing silica gel and stored at 37°C under vacuum.

The specimens were weighed repetitively using an analytical balance with 0.00001 g precision (Metter-Toledo AG285, São Paulo, SP, Brazil) each 24 hours, until a constant mass was obtained at which the variation was less than 0.2 mg in a 24-hour period (m_1) [15]. The thickness and diameter of the specimens were measured at three different points to the nearest 0.01 mm using a digital caliper. These measurements were used to calculate the volume (V) of each specimen (in mm^3). The specimens were then placed in individual microtubes containing 1.5 mL of distilled water at 37°C for 7 days. The microtubes were then removed from the incubator and left at room temperature for 30 minutes. The specimens were rapidly cleaned with soft absorbent paper and weighed in the analytical balance (m_2). Thereafter, the specimens were dried in the silica gel-containing desiccator and weighed daily until a constant mass (m_3) was obtained (as described above). Changes in mass were observed to obtain water sorption and solubility. Water sorption (W_{sp}) and solubility (W_{sl}) were calculated (μg/mm^3) by the following formulas:

$$W_{sp}: \frac{M2 - M3}{Vol}$$

$$W_{sl}: \frac{M1 - M3}{Vol}$$

Where M_1 refers to the initial dry constant mass (mg) before immersion in water; M_2 is attributed to the mass (mg) after immersion in water at various time periods; M_3 is the mass (mg) after the final drying of the specimens, and *Vol* refers to the sample volume (mm^3) [15].

After passing normality and homoscedasticity tests (data not shown), the W_{sp} and W_{sl} data were statistically analyzed using one-way ANOVA (presence of fillers) and Tukey test with a 5% significance level.

RESULTS

Microtensile bond strength (μTBS)

The outcomes of microtensile bond strength are shown in Table 1. Both the adhesives depicted

Table 1: *Means (Standard Deviations) of Microtensile Bond Strength (MPa)*[a]

	24 Hours	1 Year
Filled	48.9 (3.4) Aa	17.2 (2.6) Bb
Unfilled	46.6 (8.6) Aa	43.0 (5.8) Aa

[a] *Different capital letters in each column and lowercase letters in each row indicate statistically significant difference ($p<0.05$).*

similar bond strength at the 24-hour period (filled=48.9±3.4 MPa and unfilled=46.6±8.6 MPa). After 1 year of water storage, the unfilled adhesive (43.0±5.3 MPa) was statistically similar to the 24-hour period, but the filled group (17.2±6.2 MPa) demonstrated significant bond strength reduction ($p<0.001$).

The fracture patterns were predominantly similar and most frequently occurred in adhesive mode for all groups. However, the unfilled adhesive showed some cohesive failures in resin composite at both periods of storage. Fracture pattern outcomes are presented in Table 2.

Silver Nitrate Uptake Evaluation

The silver nitrate uptake micrographs of specimens showed similar amounts of silver deposits at interfaces of both the adhesives (Figure 1). The filled group depicted small gaps between the adhesive layer and resin composite, as well as silver impregnation in the middle of adhesive layer (Figures 1A and 1B). Although, the interfaces created in unfilled group (Figures 1C and 1D) showed more silver deposits located at the hybrid layer.

Water Sorption and Solubility

Table 3 shows the mean results of water sorption and solubility. There was higher W_{sp} for the filled adhesives (5.88±0.97 μg/mm^3) compared to unfilled adhesive (2.03±1.09 μg/mm^3), with a statistically significant difference between them ($p=0.01$). Contrariwise, W_{sl} was higher in the unfilled adhesive (8.93±1.83 μg/mm^3) compared to the filled adhesive

Table 2: *Spreading of Outcomes of Fracture Analysis After Microtensile Bond Strength Test*[a]

Type of Fracture	Filled		Unfilled	
	24 Hours (%)	1 Year (%)	24 Hours (%)	1 Year (%)
Cohesive in Composite	–	–	20	25
Mixed	6	8	4	12
Adhesive	94	92	76	63

[a] *No cohesive failure in dentin was observed in any group.*

Table 3: *Means (Standard Deviations) of Water Sorption and Solubility (μg/mm^3)*

	Water Sorption	Solubility
Filled	5.88 (0.97) B	2.94 (1.00) a
Unfilled	2.03 (1.09) A	8.92 (1.82) b

[a] *Different capital letters for water sorption results and different lowercase letters for solubility outcomes indicate statistically significant difference ($p<0.05$).*

(2.94±1.01 μg/mm^3), with a statistically significant difference between them ($p=0.008$).

DISCUSSION

Multiple methods are used to assess the longevity of bonding interfaces. This study performed the storage of resin–dentin-bonded sticks in distilled water during 1 year for microtensile bond strength assessment of bonding durability. The long-term bond strength decreased significantly only for the filler-containing adhesive. Moreover, water sorption and solubility were significantly different between the adhesives. Therefore, the null hypothesis should be rejected.

In the present investigation, the same batch of commercial universal adhesive was investigated, before or after the inclusion of silanized nanofiller particles. In order to standardize the etch-and-rinse bonding technique and to provide optimal initial bond strength values, the blot-drying cotton pellet technique was employed, according to previous literature.[17,18] It is noteworthy that the immediate bond strength of both the groups did not have any significant difference. These results are in agreement with previous studies that evaluated old versions of simplified etch-and-rinse adhesives.[11,12]

In terms of simplified adhesives, nanometer-sized silica smaller than 20 nm are usually added[19,20] and the amount of nanofiller available in commercial brands usually ranges between 5% and 10% wt%.[10] The addition of nanofillers has two intended functions—to reinforce the adhesive layer and to improve the hybrid layer with the infiltration of nanofillers into dentin tubules and into the collagen network.[21] Previous studies have shown that simplified adhesives with nanofillers may yield better mechanical properties compared with unfilled adhesive systems.[12] However, the improvement is material dependent.[12]

In terms of the hybrid layer, according to the Bertassoni and others,[22] the space between collagen fibrils is within the size of a few nanometers. This space is frequently filled with water, thereby challenging the infiltration of filler particles from

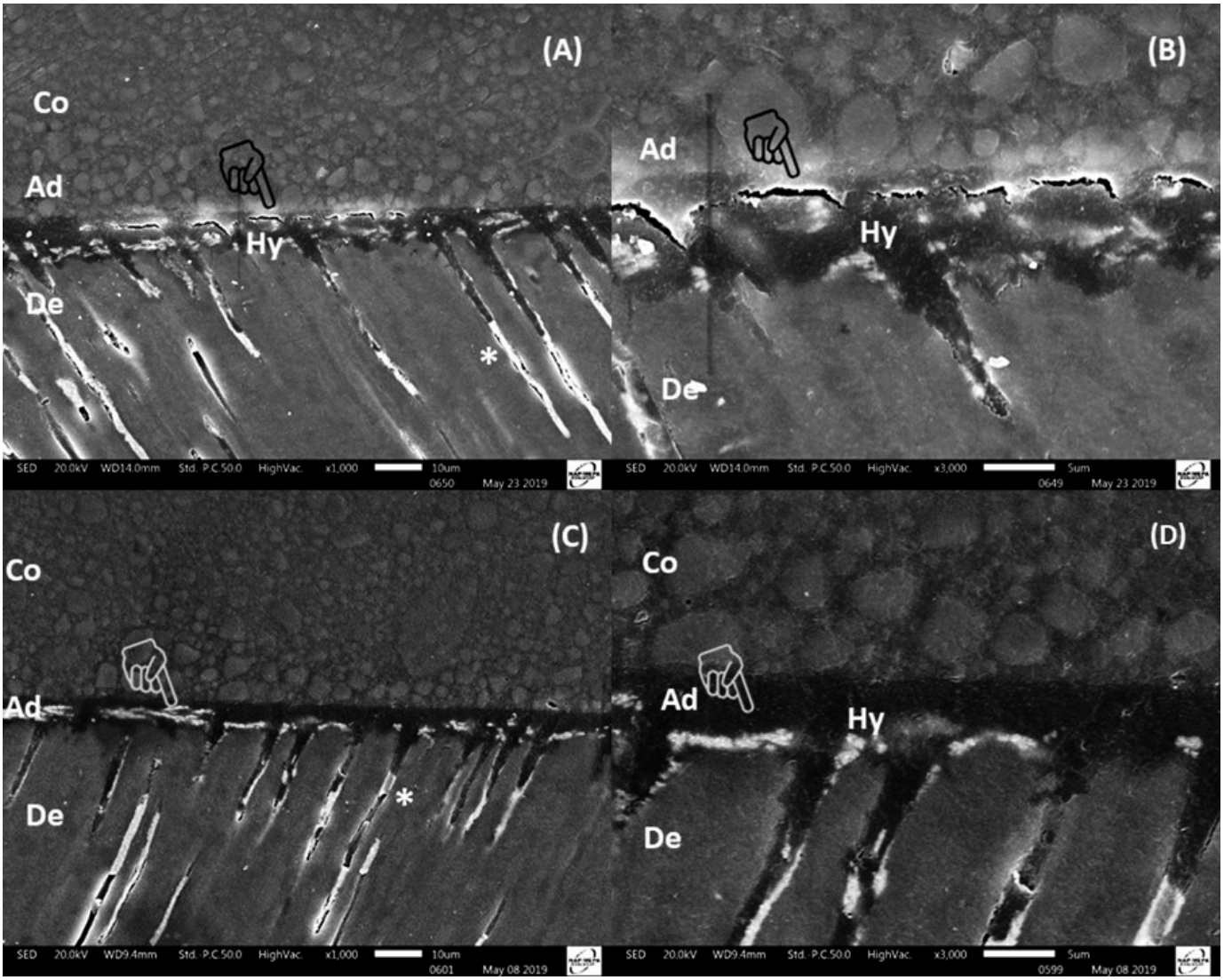

Figure 1. *Representative scanning electron microscopy (SEM) images of the silver nitrate uptake at 1000× and 3000× magnification. Ambar Universal adhesive with presence of fillers at 1000× (A) magnification and (B) at 3000×. (C) Unfilled adhesive suggests presence of water in the hybrid layer in 1000× magnification and 3000× (D). Co = resin composite; Ad = adhesive; De = dentin; Hy = hybrid layer. White arrow identifies the presence of silver at the bonding interface. Black arrow identifies the presence of gap in the resin/bond-bonding interface. *Represents presence of water in the dentinal tubules.*

adhesive into the hybrid layer properly. Unfortunately, several studies showed that no nanofiller had been found inside the hybrid layer or in the demineralized dentin, [1,21,23] mainly because the nanofiller has a tendency for aggregation, forming "filler clusters" as observed in the Figures 1A and 1B. These clusters are too large to infiltrate the collagen interfibrillar spaces.[21,24]

It is highlighted herein that a significant drop of bond strength occurred with nanofiller-containing adhesive (Table 1). On the other hand, there was bonding stability for the nanofiller-free adhesive. Indeed, this suggests that the presence of nanofiller particles is one of the triggering factors for degradation of resin–dentin interfaces, which may be an alternative to disregard the use of such nanoparticles in order to improve the durability of resin composite restorations. Nevertheless, when nanofiller particles are added to adhesive systems, the addition of a silane coupling agent is needed, which functions to promote the binding of filler particles to polymeric chains but also possesses a relatively hydrophilic nature.[10]

Therefore, the presence of a silane coating lowers the resistance to hydrolytic degradation due to the breakdown of silanol and the hydrolysis of ester

bonds from methacrylate in the presence of water.[25,26,27] Water infiltration initiates the hydrolysis of silane at the filler–polymer interfaces, thereby acting as the threshold for filler debonding and weakening of resin–dentin bonds, particularly causing the leaching of fillers.[1,2,6] Indeed, this could be confirmed by the fact that nanofiller-containing adhesive yielded higher water sorption when compared to unfilled adhesive. Yet, the presence of fillers may diminish formation of crosslinked polymeric matrix by steric impediment.[28,29]

Water seepage, polymer hydrolysis, and consequent degradation cannot be avoided, although it must be considered that in the present investigation the tiny resin–dentin-bonded sticks samples were directly stored in distilled water,[30,31] which may have increased detachment of fillers and leaching of monomers with accelerated aging of dentin–adhesive interface.[32,33]

Interestingly, although an increase in water sorption occurred for filled adhesive, the solubility decreased for filled adhesive when compared to unfilled. A suitable explanation for such an outcome is related to the presence/absence of filler particles. Solubility occurs only from resin matrix and is absent in inorganic fillers, which are insoluble. Therefore, unfilled adhesive attains higher solubility, because fillers are added usually in 5-10 wt% to filled adhesive, and these fillers do not participate in solubility of the bulk material. In other words, only 90-95% of the material is soluble in filled adhesive, whereas the unfilled adhesive possesses the entire (100%) material prone to solubilization. Thus, unfilled adhesive was indeed expected to achieve higher solubility in comparison to filled adhesive. Nevertheless, novel silane coatings have been developed to minimize the effects of hydrolytic degradation of the coupling agent by decreasing the binding strength of water to SiOH and SiO functionalities.[34,35]

In addition to the degradation of silane, water causes degradation of methacrylate in polymer chains. Monomers such as HEMA (hydroxyl-ethyl methacrylate) are often employed in simplified universal adhesives. However, HEMA is highly susceptible to water sorption and leaching due to its low molecular weight, mono-methacrylate structure, and hydrophilic feature.[32,36] Ambar adhesive (a predecessor of Ambar Universal) has shown optimal mechanical properties as compared to further commercial simplified adhesives.[37-39]

The silver nitrate uptake images revealed signs of bonding failure (small gaps) in the filled group and noteworthy presence of silver impregnation in the bonding interface of the unfilled group (Figure 1). These features are commonly observed in resin–dentin interfaces created with the most universal adhesives.[39] In addition, the greater presence of silver in the adhesive layer of the filled group is noticeable, which may be explained by the clustering of fillers (Figure 1B).

Although the vast majority of commercial adhesives contain fillers in their composition, the present investigation suggests their presence may impair optimal dentin bond durability by increasing the water sorption. Therefore, if manufacturers still demand addition of fillers to universal adhesives, new investigations should focus on the development of hydrolysis resistant hydrophobic silane molecules to maintain the benefits on adhesive mechanical properties as well as using specific techniques to produce nonaggregated nanoparticles.[41,42] Particularly, we suggest the addition of fillers with antimicrobial and remineralizing characteristics.[42,43]

CONCLUSIONS

Within the limitations of this investigation and considering that a single universal adhesive was surveyed, one may draw the conclusions that the presence of nanofiller particles in a commercial universal adhesive, applied in etch-and-rinse bonding strategy, may lead to loss of bond strength to dentin and higher water sorption compared to the same unfilled material.

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Regulatory Statement

IRB approval: "This study was conducted in accordance with all the provisions of the human subjects' oversight committee guidelines and policies. The approval code issued for this study is 011133/2018.

Conflict of Interest

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

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