



SCIREA Journal of Materials

<http://www.scirea.org/journal/Materials>

May 16, 2023

Volume 8, Issue 2, April 2023

<https://doi.org/10.54647/materials430226>

Effectiveness of two adhesive universal with functional monomers on enamel and dentin with different application modes

Carolina Gealh Navarro Escobar¹, John Alexis Dominguez², Giovana Mongruel Gomes¹, Diego Alonso Melendez Murillo³, Bruna Fortes Bittencourt¹, João Carlos Gomes¹

¹ Department of Dentistry, School of Dentistry, State University of Ponta Grossa. Ponta Grossa, Paraná, Brazil

² Department Social dentistry, Faculty of Stomatology, Universidad Peruana Cayetano Heredia, Lima, Peru.

³ Faculty of Stomatology, Universidad Peruana Cayetano Heredia, Lima, Peru.

***Correspondence:** John Alexis Dominguez, Ph.d. <https://orcid.org/0000-0002-8214-6171>
Faculty of Stomatology, Universidad Peruana Cayetano Heredia, Av. Honorio Delgado 430, San Martín de Porres, Lima and 15012, Peru
Email: john.alexis.dominguez@upch.pe, Tel: +513190000, Fax: +513190083

Abstract

Purpose: evaluated the effectiveness of the 3D-SR monomer in comparison with the 10-MDP monomer in bond strength (enamel and dentin), nanofiltration (dentin) with application of conventional and self-conditioning modes, sorption and solubility. **Materials and methods** Seventy-two molars were randomly divided into six groups according to the type of monomer of the adhesives: two adhesives with the functional 10-MDP monomer and one adhesive with the functional 3D-SR monomer, namely, Ambar Universal (AU), Single Bond Universal (SU) and Palfique Bond (PU), respectively, which were associated with the conditioning mode of

the substrates. Thirty teeth were selected for the dentin microtensile bond strength test. For microshear bond strength analysis, four flat enamel surfaces of 42 selected teeth were exposed. After preparation of the substrates, the adhesives were applied and then restored with composite resin. For the sorption and solubility samples, a cylindrical metallic matrix was used. Ten matrices were prepared for each adhesive. All data were submitted to a two-way statistical analysis (ANOVA) with Tukey's posttest ($P = 0.05$). **Results:** It was observed that the adhesives with the 10-MDP monomer showed better results of bond strength both in dentin and enamel regardless of the type of application and that the PU adhesive with the 3D-SR monomer showed lower results of bond strength independent of the substrate with self-etching application mode. **Conclusion:** The 10-MDP monomer showed the best bond strength results when applied in a self-etching mode regardless of the substrate compared to the adhesive with 3D-SR.

Keywords: Dentin adhesives, tensile strength, scanning electron microscopy, microshear, functional monomers.

Introduction

The main objective of the adhesive system is to achieve intimate contact between the dental structure and the restorative materials¹³, promoting micromechanical retention, involving two phases: removal of calcium phosphates, exposing microporosity and infiltration and subsequent polymerization of the resin inside the surface microporosity. The development of new adhesive systems tries to simplify the connection steps through its application³⁰. In general, adhesive systems consist of hydrophobic and hydrophilic resin monomers, solvents, initiators, inhibitors, and filler particles²⁸. These systems can be classified into two categories according to different application modes: conventional and self-etching²³.

Universal adhesives, recently introduced in the dental market, provide the operator with the option to select the adhesive strategy by the application mode: conventional, self-etching, or selective^{9,19,4}. Universal adhesives promise a specific chemical interaction capable of achieving a more stable and lasting adhesion. Without additional preparation of the teeth, they are similar to self-etching one-step adhesives; however, they have a more complex formulation. Simplification of one-step self-etching adhesives was made possible by increasing the amount of solvents and hydrophilic functional monomers¹⁵.

The functional monomers present in universal adhesives can simultaneously demineralize and infiltrate the dental surface, and the chemical and morphological characteristics of the adhesive-dentin substrate interface are closely related to the hybrid layer that depends to a large extent on the interaction between the functional monomers and the dental substrate ³⁴. These adhesives dissolve the smear layer and do not remove calcium phosphates. The difference between these adhesives is especially in relation to water content, acidity ¹⁰, different structures, and concentrations of functional monomers, producing different adhesive interfaces, which may have a direct impact on adherence effectiveness ³⁴.

The self-etching method of application reduces the time of application of acid washing followed by drying, as is the case with conventional adhesives. In addition, self-etching adhesives are less sensitive to the technique and promote a reduction in postoperative pain ²². Most universal adhesives are recommended by manufacturers to be applied in the self-etching mode and have the advantage of being able to bond to different restorative materials, including zirconia, metal and silica-based ceramics ².

Universal adhesives that present the 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) monomer in their formula have shown satisfactory results ^{11,31}. This monomer has an acid monomer allowing its use in the self-etching mode, which can be applied to enamel and dentin after conditioning with 35% phosphoric acid ¹¹. Other types of functional monomers (phosphate, phosphonate, carboxylic), as well as 10-MDP, are currently available on the market since they represent the main active components of self-etching adhesives, conditioning and preparing the dental substrate simultaneously, initiating the diffusion of comonomers ¹⁶. Currently, a poorly studied 3D-SR monomer (3D monomer self-reinforced with phosphoric acid) has been introduced into a universal adhesive because it has the potential for chemical bonding to the tooth structure through multiple point interactions with calcium ²⁶. The group of functional monomers generally exhibits hydrophilic properties, with the purpose of improving the humidification and demineralization of dentin, making evident the increase in bond strength of adhesives to dentin by its hydrophilic properties ²⁸.

The presence of organic solvents and acid monomers in the formulation of these new universal adhesives raises concern about their water sorption, which is one of the most important factors responsible for the degradation of the adhesive ²². There is still doubt about the adhesion durability, structural stability, formulation stability and mechanical properties over time ². However, studies show that not all universal adhesives undergo hydrolytic degradation over time, which affects their bonding durability, suggesting that the specific

composition, rather than the type of adhesive, is responsible for the adhesion performance ³³. To date, studies have confirmed that the modified 10-MDP monomer is the best acid functional monomer, showing stability and durability for both enamel and dentin ^{7,29}.

The chemical composition of the adhesives determines their clinical success. The improvement of clinical performance can be achieved by two methods: the first is to adjust the proportional amount of ingredients of the adhesives, and the other is by inserting new components ²⁸. In an effort to evaluate new functional monomers that present better or equal results to the 10-MDP monomer, the objective of this study was to evaluate the effectiveness of the little-studied functional monomer (3D-SR) compared to other adhesives containing 10-MDP through different application modes (conventional and self-etching) and different substrates (enamel and dentin), in addition to the sorption and solubility of the different adhesive systems.

Materials and methods

The experiments were approved by the Research Ethics Committee. Seventy-two healthy teeth were randomly divided according to the type of adhesive monomer: two adhesives with functional 10-MDP monomer and one adhesive with functional 3D-SR monomer, namely, (1) Ambar Universal (AU) - [FGM Prod. Odont. Ltda, Joinville, SC, Brazil], (2) Single Bond Universal (SU) - [3M ESPE, St. Paul, MN, USA], and (3) Palfique Bond (PB) - [Bond Force, Tokuyama, Osaka, Japan], respectively, which were associated with the substrate conditioning mode (enamel/dentin) and used according to the instructions shown in Table 1.

Table 1. Materials Used and application strategy

Adhesive	Manufacturer	Composition	Application Strategy	
			Self-Etch (SE)	Etch-Rinse (ER)
AMBAR UNIVERSAL	FGM	MDP, UDMA, HEMA monomer, dimethacrylate resins, ethanol, water, sodium fluoride, ethanol, initiators, silane	Apply two layers with a microbrush actively for 20 s (10 s each layer); 2. Dry carefully with a jet air for 10 s; 3. Photoactivate for 10	1. Apply the acid for 15 s; 2. Rinse thoroughly; 3. Remove excess water with air jet; 4. Apply the same adhesive as

			s.	in self-etching mode.
Palfique Bond	Tokuyama	Phosphoric acid monomer, Bisphenol A di(2-hydroxy propoxy) dimethacrylate (Bis-GMA), Triethylene glycol dimethacrylate, 2-Hydroxyethyl methacrylate (HEMA), Camphorquinone, alcohol	1. Apply two layers of adhesive actively for 20 s; 2. Wait 10 s. 3. Dry carefully with jets and air for 5 s. Photoactivate by 10 sec.	1. Apply the acid for 15 s; 2. Rinse for 10 s; 3. Remove excess water with air jet for 2 s; 4. Apply the same adhesive as self-etching mode.
Scotchbond UNIVERSAL	3 M ESPE	MDP, Monomer, dimethacrylate, HEMA, methacrylate-modified polyalkenoic acid copolymer, filler, ethanol, water, initiators, silane.	1. Apply the adhesive actively for 20 s and if necessary reapply the adhesive; 2. Dry carefully with a jet of air for 5 s, until the adhesive does not move and just solvent evaporate completely 3. Light curing for 10 s at 1200 mW/cm ² .	1. Apply the acid for 15 s; 2. Rinse for 10 s; 3. Remove excess water with air jet for 2 s; 4. Apply the same adhesive as self-etching mode.

Preparation of samples for microshear

For analysis of the microshear test, four flat enamel surfaces of 42 selected teeth were exposed (buccal, lingual and proximal) after wearing the enamel surface with SiC granulation paper # 180 for 60 seconds under constant water irrigation; for standardization of the enamel surface, SiC granulation paper # 600 and # 1200 after for 60 seconds was used. After removing the roots and then fixing them on a device for adaptation on the Isomet Low Speed Saw manual cutting machine (South Bay Technology Inc. Buehler, Lake Bluff, IL, USA), a diamond blade under refrigeration was selected (Exttec Dia, Wafer blade 5 "x. 015x1/2, Exttec

Corp, Enfield, CT, USA) to section the crown longitudinally in two cuts in the mesial-distal and distal-mesial directions, obtaining 4 fragments of teeth.

Before applying the adhesive, the fragments were inserted in a polyvinyl chloride ring fixed with chemically activated acrylic resin (AutoClear, DentBras, Pirassununga, São Paulo, Brazil), showing the enamel surface at the top of the cylinder, which was polished with silicon carbide sandpaper progressively with granulation # 400 and # 600 for 60 s. On the sample surface, double-sided adhesive tape (Adelbras Ind e Com Adhesives Ltda, São Paulo, Brazil) perforated with a Hygenic Ainsworth rubber dam punch (Coltene, Alstätt, Switzerland) was placed. The 4 fragments were randomly divided to apply a different adhesive system, respecting the manufacturer's instructions and the different strategies of the application method standardized by the present study. Tygon polyethylene tubes (Tygon Medical Tubing Formulations 54-HL, Saint Gobain Performance Plastics, Akron, OH, USA) with an internal diameter of 0.8 mm were sectioned to obtain 0.5 mm high matrices. A second side section was made to reduce the outside diameter of the matrix. Each matrix was placed on double-sided tape with the lumen coinciding with a perforation. The operator trained in the μ TBS technique positioned three to four restorations per fragment.

The composite resins were carefully inserted into each tube, and a clean Mylar matrix was placed over the tube filled with resin and gently pressed. The resins were light-cured for 20 s, and all restorative procedures were performed with a 5x magnifying glass. After storing the restored teeth in distilled water for 24 hours at 37 °C, the Tygon tubes and double-sided adhesive tape were carefully removed, exposing the composite resin cylinders. Each sample was examined under a 100x stereomicroscope (Olympus SZ40, Tokyo, Japan) to identify samples with evidence of air bubbles or gaps in the interface, which were discarded.

For the test, the samples were submitted to a microshear test (Odeme Biotechnology, Joinville, Brazil) and tested on a universal testing machine (Kratos IKCL 3-USB, Kratos Equipamentos Industriais Ltda, Cotia, São Paulo, Brazil). A wire (0.2 mm in diameter) was connected around the base of each composite cylinder, making contact with half of its circumference, keeping the connection aligned at the resin-enamel interface, the wire connection and the center of the cell load to ensure the correct orientation of the shear force. A shear load was applied at a speed of 1 mm/min until failure. The μ SBS values were calculated by dividing the failed load by the surface area (mm²) to determine the shear force connection in MPa.

Preparation of samples for microtensile testing

Thirty teeth were used for the dentin microtensile bond strength test. All enamel on the occlusal surface was removed, and after exposure of the dentin surface, silicon carbide (SiC) sandpaper was used until an enamel-free surface was obtained. The side enamel was worn with a high-speed diamond bur under constant irrigation, leaving only dentin tissue. To standardize the smear layer, silicon carbide (SiC) sandpaper was used with water irrigation for 60 s.

The adhesive system was applied according to the manufacturer's instructions (Table 01) and study standardization. After the adhesive procedure, all teeth received a composite resin restoration (Opallis, FGM Prod. Odont. Ltda, Joinville, SC, Brazil) with two increments of 2 mm at a time. Each increment was light-cured for 40 seconds with an LED light curing unit set at 1200 MW/cm² (Radii-cal, SDI Limited, Bayswater, Victoria, Australia). A radiometer (Demetron LED Radiometer, Kerr Sybron Dental Specialties, Middleton, WI, USA) was used to evaluate the light intensity after five samples.

After storing the restored teeth in distilled water at 37 °C for 24 hours, the samples were sectioned longitudinally in the mesio-distal and bucco-lingual directions through the union interface with a low-speed diamond disc (Isomet, Buehler Ltd, Lake Bluff, IL, USA) to obtain dentin and composite resin sticks with a cross-sectional area of approximately 0.8 mm, which were measured with a digital caliper (Digimatic Caliper, Mitutoyo, Tokyo, Japan). Three sticks of each tooth, which were not tested by μ TBS, were used for the nanofiltration test. The resin-dentin interface sticks were fixed in a Geraldeli jig40 claw (Odeme Biotechnology, Joaçaba, Santa Catarina, Brazil) with cyanoacrylate adhesive, which was attached to a universal testing machine (Kratos Cotia, São Paulo, Brazil) and pulled until fracture at a speed of 0.5 mm/min. Most peripheral sticks were discarded. The μ TBS values were calculated by dividing the failure load by the cross-sectional area.

Analysis of nanofiltration by scanning electron microscopy.

Three random sticks from each tooth that were not tested for μ TBS were immersed in an ammoniacal solution of silver nitrate at 50% by weight for 24 h in a dark environment protected from light. Then, the samples were washed in distilled water and stored in a revealing solution (Kodak, Rochester, New York, USA) under fluorescent light for 8 h so that there was a reduction of silver ions along the microporosities at the union interface. Then, the

samples were fixed in aluminum stubs and polished with # 600, # 1000, # 1200, # 1500, # 2000 and # 2500 SiC sandpaper and 1 and 0.25 μm diamond pastes (Buehler Ltd., Lake Bluff, IL, USA), with an ultrasonic bath between the sandpapers for 5 min. Subsequently, the stubs containing the samples were washed in an ultrasonic bath for 30 min, dehydrated in an environment containing silica and metalized with gold-carbon (MED 010, Balzers Union, Balzers, Liechtenstein) (Figure 4). The interfaces were observed by scanning electron microscopy (SEM) in electron scattering mode at 12 kV (VEGA 3 TESCAM, Shimadzu, Tokyo, Japan) and 600x magnification.

Three microphotographs were obtained for each sample: the first at the center, and the other two at 0.3 mm to the right and left from the first microphotograph. The percentage of nanofiltration within the adhesive and hybrid layers was measured by specific public domain software (ImageJ software program version 1.42q; NIH, Bethesda, MD).

Sorption and solubility tests

A cylindrical metallic matrix (5.0 mm in diameter, 1.0 mm thick; Odeme Prod Odont Ltda, Joaçaba, SC, Brazil) was used to make the samples (CPS). Ten CPS were made for each adhesive. Vaseline was applied to the base of the matrix, and then a polyester matrix was placed in contact with the base of the matrix.

Excess Vaseline over the matrix was removed, and after the matrix was displaced, each type of adhesive was dripped into the matrix until complete filling. All visible air bubbles from the adhesives were carefully removed with the aid of a microapplicator or probe (Microbrush® FGM, Prod. Odont. Ltda, Joinvile, SC, Brazil). Evaporation of the solvent was carried out with a jet of air for 40 s at a distance of 10 cm.

Another polyester strip was placed over the matrix, and the adhesives were light-cured for 40 s with the Radium-cal LED. light curing unit (SDI, Bayswater, Victoria, Australia) with an intensity of 1200 mW/cm².

The samples were carefully removed from the matrix with the aid of a scalpel blade, and all burrs of adhesive were also removed. The CPS allowed its removal from the metal matrix without suffering permanent deformations.

Then, they were placed in a desiccator (EP with silica gel on the bottom and gauze over the silica) and transferred to an oven at 37 °C. After 24 h, the samples were periodically weighed on an analytical scale until a uniform mass was obtained, that is, m1 (the loss of mass of the sample was less than 0.1 mg between two consecutive periods of 24 h). When this uniform

mass was reached, the thickness and diameter of the samples were measured using a digital caliper (Absolute Digimatic, Mitutoyo, Tokyo, Japan) with three decimal places of precision, and these measures were used to calculate the volume (area x thickness) of each sample in mm³ (Figure 5).

After weight stabilization, the samples were placed individually in Eppendorf tubes containing 10 mL of distilled water each and returned to the oven at 37 °C. After fixed periods of 1 h (up to 8 h) and 1, 2, 3, 4, 5, 6, 7, 14 and 28 and 56 days, the Eppendorf tubes were removed from the oven and kept at room temperature for 30 min. After each of these periods, the samples were dried with absorbent paper, weighed on an analytical scale (m₂) and returned to the distilled water.

Thus, the mass of each sample was measured hourly (up to 8 h) on the first day and daily until the seventh day, and then the mass was measured after 14 and 28 days. After the 28-day period, the samples were removed from the distilled water, stored again in Eppendorf tubes with silica gel and weighed daily until a constant mass (m₃) was obtained in the same way as described in m₁.

To obtain the volume value (m₁, m₂, m₃), three measurements were made, calculating the average between them each time. The initial mass (m₁) was used as a parameter to verify the change in the mass of each material after a fixed interval of time during the first 28 days. Water sorption (SA) and solubility (SO) over the 28-day period were calculated for each material with the following formulas:

$$SA = (m_2 - m_3)/V_e$$

$$SO = (m_1 - m_3)/V.$$

Statistical analysis

An average of the bond strength values to enamel and dentin and nanofiltration to dentin was obtained for statistical purposes so that the experimental unit in this study was the tooth. MTBS (MPa) and NI data (%) were subjected to a two-way ANOVA (application mode of the adhesive system vs. adhesive system) and Tukey test with a significance level of 5%.

Results

Microtensile and Microshear values

The means and the respective standard deviations of the bond strength test in enamel and dentin are shown in Table 2. The two-way ANOVA showed statistical significance between the following factors: adhesives vs. mode of application in dentin and adhesive vs. adhesive and adhesive vs. mode of application in enamel. Significant difference between treatments ($p < 0.001$).

Table 2. Mean and standard deviations (SD) of the shear bond strengths (MPa) in dentin (microtensile) and enamel (microshear) and application strategy.

	Microtensile		Microshear	
	application strategy			
	CC	SC	CC	SC
SU	16.91±3.56 a	19.41±3.57 a	34.77±8.25 A,a	30.96±5.98 A,a
AU	16.96±2.57 a	17.22±2.86 a	30.89±8.75 A,a	30.57±8.14 A,a
PB	15.82±2.81 a	14.74±2.25 b	31.09±8.01 A,a	24.13±4.38 B,b

means followed by different letters (uppercase in rows and lowercase in columns)

The highest average bond strength per sample group in dentin was 19.41 ± 3.57 MPa obtained by the SU/SE group, and the lowest result was in the PB/SE group at 14.74 ± 2.25 MPa. Regarding the different strategies, there was no significant difference in relation to the types of adhesives, and the SU subgroup showed a statistically higher value for the PB group.

When the bond strength in enamel was evaluated, the SU group had the lowest value with the SC application strategy (24.13 ± 4.38 MPa), which was statistically significant in relation to the other groups. With the ER strategy, the PB values did not show a significant difference in relation to the other adhesives.

Nanofiltration (NI)

Data on the means and standard deviations (%) of NI for all experimental groups are shown in Table 3. Significant differences between treatments ($p < 0.0001$), adhesive systems ($p < 0.0001$) and application mode of the adhesive ($p < 0.0001$) were observed.

It was observed that in relation to the application strategy, the PB group showed higher values of nanofiltration with the SE strategy (15.74 ± 3.32). Using the ER strategy, it was noted that only the AU group showed a statistically significant difference with higher values of nanofiltration (12.67 ± 2.86 B, b).

The lowest mean nanofiltration was observed with the SC strategy in the SU group (4.72 ± 3.26), which had the lowest nanofiltration values regardless of the application strategy (Figure 1).

Table 3. Mean and standard deviations (SD) (%) of the nanoinfiltration values obtained in each experimental condition.

Adhesives	application strategy	
	CC	SC
SU	04.77±3.32 A,a	04.72±3.26 A a
AU	12.67±2.86 B,b	15.74±3.32 B,b
PB	05.42±2.17 A,a	11.42±2.80 B,b

means followed by different letters (uppercase in rows and lowercase in columns)

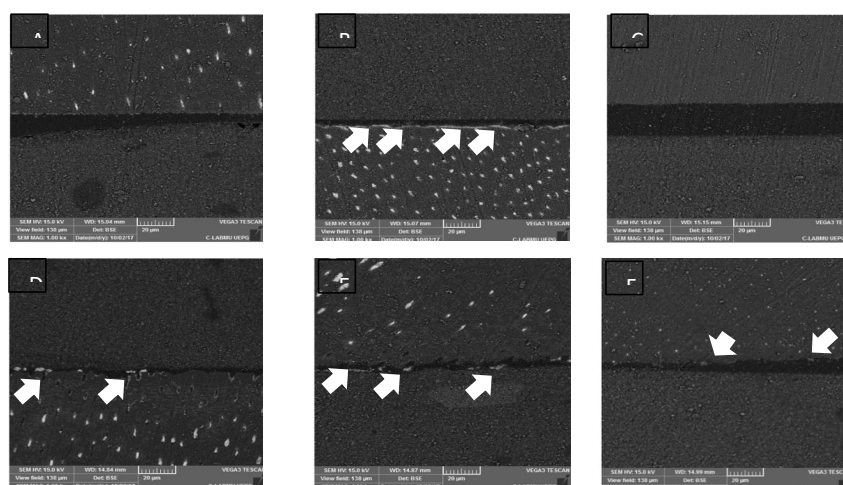


Figure 1 Nanoinfiltration: scanning electron microscopy resin/dentin interfaces A:PB-SE, B: AU-SE, C: SU-SE, D:PB-ER, E:AU-ER, E:SU-ER.

Sorption and solubility

Data on the means and standard deviations (%) of sorption and solubility for all experimental groups are shown in Table 4. A significant difference between the adhesive systems ($p \geq 0.05$) was observed.

It was observed that in relation to adhesive systems, only PB showed higher values of sorption (403.5 ± 83.9) and solubility (187.7 ± 28.0). Regarding the AU and SU adhesives, no significant difference was noticed; however, it was noticed that the lowest values of sorption and solubility were found in the SU adhesive (127.0 ± 36.4 and 64.8 ± 13.7 , respectively).

Table 4. Mean and standard deviations (SD) sorption ($\mu\text{g}/\text{mm}^3 * 10^{-6}$) and solubility ($\mu\text{g}/\text{mm}^3 * 10^{-6}$) obtained in each experimental condition (*).

	Sorption ($\mu\text{g}/\text{mm}^3 * 10^{-6}$)	Solubility ($\mu\text{g}/\text{mm}^3 * 10^{-6}$)
Adhesive	56-days	
PB	403.5 ± 83.9^B	187.7 ± 28.0^b
AU	151.8 ± 35.6^A	97.1 ± 43.6^a
SU	127.0 ± 36.4^A	64.8 ± 13.7^a
means followed by different letters (uppercase in adhesives de sorption and lowercase in solubility (Tukey's test, $p \geq 0.05$)).		

Discussion

A relatively high bond strength was found for AU and PU adhesives in both enamel and dentin, regardless of the application mode. This result can be explained by the presence of the 10-MDP monomer in its composition, which has a chemical bonding capacity for rigid tooth structures, allowing for a stable bond to dentin substrates for a long time (Reis et al. ²¹2009; Perdigao et al. ²⁸ 2014). In addition, the adhesives containing the 10-MDP monomer are less hydrophilic due to the long molecular chain, causing the interaction between 10-MDP and hydroxyapatite to form nanolayers; therefore, they are considered more adhesive (Anchieta et al. ¹ 2015).

The 10-MDP monomer forms a stable layer by depositing MDP-Ca salts on the adhesive interface, increasing its mechanical resistance and establishing a very intense and stable chemical interaction with the hydroxyapatite. The formation of water-insoluble MDP-Ca salts contributes to the protection of collagen fibers in dentin. The intense chemical interaction established between the 10-MDP monomer and hydroxyapatite is attributed to the superficial dissolution of the hydroxyapatite induced by the adsorption of 10-MDP and subsequent deposition of MDP-Ca salts with less solubility than the salts produced by other monomers.

This monomer is composed of a polymerizable methacrylate radical and a phosphoric radical. This spacer chain is the greatest justification for 10-MDP to have excellent physical and chemical properties and chemical bonding that generate greater bond strength over time. The long chain consisting of ten carbons allows the necessary balance in relation to the polarity of the molecule, compensating for the hydrophilicity of the phosphoric radical. (Van Landuyt et al. ²⁹ 2008). Each layer of this structure (nanolayer) consists of two 10-MDP molecules with their methacrylate groups directed toward each other and their functional hydrogen phosphate groups facing each other (Fukeygawa et al. ⁸ 2006); the greater the formation of the monomer-calcium molecule, the higher the bond strength and durability, in comparison with adhesives that achieve less formation of the monomer-calcium molecule (Wang et al. ³⁴ 2017).

The application of the PU adhesive for both enamel and dentin without acid etching showed lower results of bond strength. One of the reasons is related to the functional monomer of the PU adhesive, which has not yet been studied. This monomer has the potential for chemical bonding to the tooth structure, forming multipoint interactions with calcium. However, a recent study compared one-step self-etching adhesives with different types of solvents: acetone and ethanol, isopropyl alcohol and ethanol, and the sorption and solubility results were higher when the solvent of choice was isopropyl alcohol, similar to the results of our study. Any residue of the solvent after air drying can produce changes in the polymerized adhesive, later being replaced by water. The vapor pressure (at 25 °C) is 44 mm Hg for isopropyl alcohol, 200 mm Hg for acetone and 54.1 mm Hg for ethanol. Due to the low vapor pressure of isopropyl alcohol, more time is needed for its evaporation compared to ethanol, which is present in the other two adhesives, delaying its polymerization. Therefore, in the case of PU, the solvent may not have been completely removed with the air jet, causing the formation of pores in the polymerized adhesive nanolayer caused by the presence of residual solvent, allowing an increase in the results of nanofiltration and even bond strength by weakening the hybrid layer, causing a greater risk of deterioration (Turkistani et al. ²⁶ 2018) (Carvalho et al. ³ 2019).

Regarding application mode, a recent systematic review was carried out to determine the best application protocol: conventional and self-etching modes in bonding to dentin and enamel by universal adhesives. A statistically significant difference between the strategies was not observed regarding bond strength to dentin, results similar to the tested adhesives containing the 10-MDP monomer (Rosa et al. ²³ 2015). However, another study shows an increase in bond strength when the adhesive is applied in the conventional way in only some of the tested

universal adhesives (Walter et al. ³³ 2012), concluding, therefore, that the method of application is not the only factor that influences bond strength results. Another systematic review demonstrates that the bond strength was higher with the conventional application mode, being more suitable to use selective conditioning because it produces macro- and micropores on the enamel surface resulting from the dissolution of hydroxyapatite, increasing the surface area of the substrate (Cuevas-Suarez et al. ⁶ 2019), diverging from the results of the universal adhesives containing 10-MDP monomer from the present study.

The application of self-etching adhesives on the enamel is associated with some concerns, such as the pattern of superficial etching of the enamel and the reduction in micromechanical retention over time (Pouyanfar et al. ²⁰ 2018), which goes against the result of the PU adhesive when applied in self-etching mode. However, an 18-month clinical trial that evaluated a universal adhesive with conventional and self-etching applications revealed that the bond strength of Scotchbond Universal does not depend on the bonding strategy (Turkun ²⁷ 2005). In the present study, both the SU and AU adhesives did not show a difference between the application modes, similar to the results obtained with adhesives that have 10-MDP in the present study.

The higher values in the results of nanofiltration regardless of the application mode for the AU adhesive lead us to believe, in addition to previous results (Wagner et al. ³² 2014); (Takamizawa et al. ²⁵ 2016), that the results of nanofiltration do not correlate with the results of bond strength. Other studies show that even after 6 months with increased nanofiltration, the bond strength has not been altered (Munoz et al. ¹⁴ 2015). In addition to the good results of bond strength and sorption and solubility, the Scotchbond Universal adhesive obtained the best results of nanofiltration regardless of the conditioning mode, which can be attributed to its chemical composition. In addition to containing 10-MDP in its composition, it has a polyalkenoic acid copolymer modified with methacrylate (Munoz et al. ¹⁴ 2015; Manhart et al. ¹² 2004), which has similar characteristics of chemical bonding to hydroxyapatite (Sezinando et al. ²⁴ 2016), thus increasing the bond strength.

Studies show that the bonding of an adhesive with CAP is higher than that of an adhesive without CAP with the same composition (Perdigao et al. ¹⁸ 2014). The 10-MDP long hydrophobic chain, keeping the presence of water away together with the stable 10-MDP-Ca nanolayer, can effectively protect the adhesive interface together with the polyalkenoic acid that binds chemically and spontaneously to HAp. The basic difference between polyalkenoic acid and 10-MDP is that 10-MDP contains individual monomers that after polymerization

become a polymer bound to HAp, while polyalkenoic acid is a polymer with several carboxylic functional groups attached to the polymer backbone and can connect to Ca in more remote locations (Manhart et al. ¹² 2004).

The application mode, type and amount of solvent and pH, composition and percentage of monomers, amount of charge, percentage of mass charge, different diluents, presence and quantity of hydrophilic and hydrophobic monomers, viscosity of the adhesive, intermolecular termination rate, and length of the primary chain, among other constituents of the various adhesives, can affect the results of bond strength (Pouyanfar et al. ²⁰ 2018; Sezinando et al. ²⁴ 2016). The presence and quantity of HEMA, a hydrophilic monomer, directly affects water absorption, increasing its sorption proportionally by its quantity (Nishitani et al. ¹⁷ 2007). In addition to the water added to the adhesive to trigger the ionization of the respective monomer in the self-etching mode, all adhesives used in this study contain an organic solvent. The solvents act as carriers of the monomers in the collagen interfibrillar spaces and as diluents to reduce the viscosity of the resin. The volatilization of the solvent facilitates the polymerization reaction by reducing the distance between monomers, increasing the degree of conversion and, consequently, the bond strength (Chen and Suh ⁵ 2013).

The working process of adhesive interfaces involves a sequence of events, which cannot yet be fully understood, and different structures; consequently, different concentrations of functional monomers produce adhesive interfaces with particular chemical and morphological substances that have a direct impact on the effectiveness of adhesion (Wang et al. ³⁴ 2017) ^{3,2}.

Conclusion

The results showed that further studies regarding the 3D-SR monomer still need to be carried out. The functional 10-MDP monomer showed better results regardless of the dental substrate or application mode in the bond strength values. The AU adhesive showed higher results of nanofiltration, without correlation with the results of bond strength and sorption and solubility. The PB adhesive showed a decrease in bond strength when applied in a self-etching mode and higher results of sorption and solubility.

References

- [1] Anchieta RB, Machado LS, Martini AP, Santos PH, Giannini M, Janal M, et al. Effect of long-term storage on nanomechanical and morphological properties of dentin-adhesive interfaces. *Dental materials* 2015;31:141-153.
- [2] Bahrololumi N, Beglou A, Najafi-Abbrandabadi A, Sadr A, Sheikh-Al-Eslamian SM, Ghasemi A. Effect of water storage on ultimate tensile strength and mass changes of universal adhesives. *Journal of clinical and experimental dentistry* 2017; 9:e78-e83.
- [3] Carvalho CN, Lanza MDS, Dourado LG, Carvalho EM, Bauer J. Impact of Solvent Evaporation and Curing Protocol on Degree of Conversion of Etch-and-Rinse and Multimode Adhesives Systems. *International journal of dentistry* 2019:5496784.
- [4] Chen C, Niu LN, Xie H, Zhang ZY, Zhou LQ, Jiao K, et al. Bonding of universal adhesives to dentine--Old wine in new bottles?. *Journal of dentistry* 2015;43:525-536.
- [5] Chen L, Suh BI. Effect of hydrophilicity on the compatibility between a dual-curing resin cement and one-bottle simplified adhesives. *The journal of adhesive dentistry* 2013;;15:325-331.
- [6] Cuevas-Suarez CE, da Rosa WLO, Lund RG, da Silva AF, Piva E. Bonding Performance of Universal Adhesives: An Updated Systematic Review and Meta-Analysis. *The journal of adhesive dentistry* 2019;21:7-26.
- [7] Fujita K, Ma S, Aida M, Maeda T, Ikemi T, Hirata M, et al. Effect of reacted acidic monomer with calcium on bonding performance. *Journal of dental research* 2011; 90:607-612.
- [8] Fukegawa D, Hayakawa S, Yoshida Y, Suzuki K, Osaka A, Van Meerbeek B. Chemical interaction of phosphoric acid ester with hydroxyapatite. *Journal of dental research*. 2006; Oct;85(10):941-4.
- [9] Kalavacharla VK, Lawson NC, Ramp LC, Burgess JO. Influence of Etching Protocol and Silane Treatment with a Universal Adhesive on Lithium Disilicate Bond Strength. *Operative dentistry* 2015;40:372-378.
- [10] Loguercio AD, Munoz MA, Luque-Martinez I, Hass V, Reis A, Perdigao J. Does active application of universal adhesives to enamel in self-etch mode improve their performance? *J Dent* 2015;43:1060-1070.

- [11] Manfroï FB, Marcondes ML, Somacal DC, Borges GA, Junior LH, Spohr AM. Bond Strength of a Novel One Bottle Multimode Adhesive to Human Dentin After Six Months of Storage. *The open dentistry journal* 2016;10:268-277.
- [12] Manhart J, Chen H, Hamm G, Hickel R. Buonocore Memorial Lecture. Review of the clinical survival of direct and indirect restorations in posterior teeth of the permanent dentition. *Operative dentistry* 2004;29:481-508.
- [13] Masarwa N, Mohamed A, Abou-Rabii I, Abu Zaghlan R, Steier L. Longevity of Self-etch Dentin Bonding Adhesives Compared to Etch-and-rinse Dentin Bonding Adhesives: A Systematic Review. *The journal of evidence-based dental practice* 2016;16:96-106.
- [14] Munoz MA, Luque-Martinez I, Malaquias P, Hass V, Reis A, Campanha NH, et al. In vitro longevity of bonding properties of universal adhesives to dentin. *Oper Dent* 2015;40:282-292.
- [15] Munoz MA, Sezinando A, Luque-Martinez I, Szesz AL, Reis A, Loguercio AD, et al. Influence of a hydrophobic resin coating on the bonding efficacy of three universal adhesives. *Journal of dentistry* 2014; 42:595-602.
- [16] Nishiyama N, Suzuki K, Takahashi K, Nemoto K. The pKa effects of the carboxylic acid in N-methacryloyl-omega-amino acid on the demineralization and bond strengths to the teeth. *Biomaterials* 2004;25:5441-5447.
- [17] Nishitani Y, Yoshiyama M, Hosaka K, Tagami J, Donnelly A, Carrilho M, et al. Use of Hoy's solubility parameters to predict water sorption/solubility of experimental primers and adhesives. *European journal of oral sciences* 2007;115:81-86.
- [18] Perdigao J, Munoz MA, Sezinando A, Luque-Martinez IV, Staichak R, Reis A, et al. Immediate adhesive properties to dentin and enamel of a universal adhesive associated with a hydrophobic resin coat. *Oper Dent* 2014;;39:489-499.
- [19] Perdigao J, Kose C, Mena-Serrano AP, De Paula EA, Tay LY, Reis A, et al. A new universal simplified adhesive: 18-month clinical evaluation. *Operative dentistry* 2014;39:113-127.
- [20] Pouyanfar H, Tabaii ES, Aghazadeh S, Nobari S, Imani MM. Microtensile Bond Strength of Composite to Enamel Using Universal Adhesive with/without Acid Etching Compared To Etch and Rinse and Self-Etch Bonding Agents. *Open access Macedonian journal of medical sciences* 2018; 25;6:2186-2192.

- [21] Reis A, Leite TM, Matte K, Michels R, Amaral RC, Geraldeli S, et al. Improving clinical retention of one-step self-etching adhesive systems with an additional hydrophobic adhesive layer. *J Am Dent Assoc* 2009;140:877-885.
- [22] Reis A, Wambier L, Malaquias T, Wambier DS, Loguercio AD. Effects of warm air drying on water sorption, solubility, and adhesive strength of simplified etch-and-rinse adhesives. *The journal of adhesive dentistry* 2013;15:41-46.
- [23] Rosa WL, Piva E, Silva AF. Bond strength of universal adhesives: A systematic review and meta-analysis. *J Dent* 2015;43:765-776.
- [24] Sezinando A, Serrano ML, Perez VM, Munoz RA, Ceballos L, Perdigao J. Chemical Adhesion of Polyalkenoate-based Adhesives to Hydroxyapatite. *J Adhes Dent* 2016;18:257-265.
- [25] Takamizawa T, Barkmeier WW, Tsujimoto A, Berry TP, Watanabe H, Erickson RL, et al. Influence of different etching modes on bond strength and fatigue strength to dentin using universal adhesive systems. *Dent Mater* 2016;32:e9-21.
- [26] Turkistani A, Almutairi M, Banakhar N, Rubehan R, Mugharbil S, Jamleh A, et al. Optical Evaluation of Enamel Microleakage with One-Step Self-Etch Adhesives. *Photomedicine and laser surgery* 2018; 36:589-594.
- [27] Turkun LS. The clinical performance of one- and two-step self-etching adhesive systems at one year. *Journal of the American Dental Association*. 2005; May;136(5):656-64; quiz 83.
- [28] Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A, et al. Systematic review of the chemical composition of contemporary dental adhesives. *Biomaterials* 2007;28(26):3757-3785.
- [29] Van Landuyt KL, Yoshida Y, Hirata I, Snauwaert J, De Munck J, Okazaki M, et al. Influence of the chemical structure of functional monomers on their adhesive performance. *Journal of dental research* 2008;87:757-761.
- [30] Van Meerbeek B, De Munck J, Yoshida Y, Inoue S, Vargas M, Vijay P, et al. Buonocore memorial lecture. Adhesion to enamel and dentin: current status and future challenges. *Operative dentistry* 2003; 28:215-35.

- [31] Vermelho PM, Reis AF, Ambrosano GMB, Giannini M. Adhesion of multimode adhesives to enamel and dentin after one year of water storage. *Clinical oral investigations* 2017; 21:1707-1715.
- [32] Wagner A, Wendler M, Petschelt A, Belli R, Lohbauer U. Bonding performance of universal adhesives in different etching modes. *J Dent* 2014;;42:800-807.
- [33] Walter R, Swift EJ, Jr., Nagaoka H, Chung Y, Bartholomew W, Braswell KM, et al. Two-year bond strengths of "all-in-one" adhesives to dentine. *Journal of dentistry* 2012;40:549-555.
- [34] Wang R, Shi Y, Li T, Pan Y, Cui Y, Xia W. Adhesive interfacial characteristics and the related bonding performance of four self-etching adhesives with different functional monomers applied to dentin. *Journal of dentistry* 2017; 62:72-80.