

Influence of acidic monomer concentration and application mode on the bond strength of experimental adhesives

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Abstract: The aim of this research was to evaluate the influence of MDP (10-methacryloyloxydecyl dihydrogen phosphate) concentration and application mode of experimental adhesives on microshear bond strength (μ SBS) to dentin after storage in distilled water at 37°C for 24h and 6 months. Five experimental adhesives were prepared with: CQ, DABE, BHT, ethanol, HEMA, TEGDMA, Bis-EMA, UDMA, and Bis-GMA. Concentrations of 0 wt%, 3 wt%, 9 wt%, 12 wt% or 15 wt% of MDP were added to their composition. The adhesives were applied to flat dentin surfaces in etch-and-rinse or self-etching modes. Cylindrical molds filled with light-cured composite resin were placed above the dentin. The specimens were stored in distilled water at 37°C for 24h or 6 months and submitted to μ SBS testing. The adhesives were also submitted to pH analysis. The data were analyzed by one-way ANOVA, three-way ANOVA and Tukey's test ($\alpha = 5\%$). All the adhesives used in the etch-and-rinse mode showed significantly higher bond strength than the adhesives applied in the self-etching approach. The 9 wt% adhesive showed the highest bond strength values, and 3 wt% was most stable after storage. A strong negative correlation between MDP concentration and pH was observed. It was concluded that the formulations with low concentrations of MDP (up to 9 wt%) showed better results for bond strength and bond strength degradation over time.

Keywords: Dental Bonding; Dentin-Bonding Agents; Adhesives; Dental Materials.

Introduction

Functional monomers can make the bond strength more resistant and durable between composite resin and adhesive systems, and between adhesive systems and tooth structures.¹ Among these monomers, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) is an ester of acidic constitution that forms a low solubility calcium salt, capable of interacting with hydroxyapatite by chemical bonding to the Ca^{2+} ions in the collagen fibrils or the hybrid layer, in forming MDP-Ca salt.^{2,3,4,5} The deposition of MDP-Ca salt produces an acid-resistant zone, since this salt increases the



resistance to solubility significantly, compared with the salts produced by other functional monomers.^{3,6,7,8}

The characteristics of a dental adhesive formulation can influence its effectiveness directly. Among these characteristics, the pH and amount of water in the adhesive system can influence smear layer removal. Water functions as an ionizing medium in the bonding of the released Ca²⁺ ions to the MDP molecule, forming the MDP-Ca salt.⁹ The amount of water in MDP-based adhesives plays a role in the bond strength to dentin. An increase in the amount of water in experimental adhesives has been found to increase their ability to demineralize and remove the smear layer.⁹ However, dentin solubilization decreased the bond strength before and after thermocycling.⁹

Adhesive procedures require smear layer treatment to increase the interaction with the dental substrate. Whereas the smear layer is completely removed by acid etching with etch-and-rinse adhesives, self-etching adhesives need a different approach, based on the pH of the primer or bonding agents. On the other hand, universal adhesives are similar to single-bottle one-step self-etch adhesive systems, and can be used with etch-and-rinse, self-etching, or selective enamel-etching modes.¹⁰ Self-etching adhesives are classified according to their acidity as follows: strong (pH ≤ 1), intermediate (pH ~ 1.5), and mild (pH ≥ 2).¹ A new group of self-etching adhesives called “ultra-mild” have been introduced on the market. These adhesives have low acidity (pH ~ 2.7). This pH value promotes reduced smear layer dissolution, and allows a thin smear layer to be obtained.^{11,12} The pH plays a major role, since it has been shown that bond strength to dentin is increased when ultra-mild MDP-containing universal adhesives are used with the etch-and-rinse technique.^{13,14}

Incorporation of MDP into the formulation of adhesive systems has been found to significantly improve their bond strength and reduce hybrid layer degradation over time.^{15,16,17} Some studies have evaluated the bond strength of adhesives containing different concentrations of MDP in an attempt to correlate these different concentrations of functional monomers to bond strength to dentin;^{8,18,19,20} however, the data are still inconclusive, and the ideal

concentration of MDP for adhesive systems could not as yet be established. Functional monomers such as MDP may interact with the amine from the CQ/amine light activation system through an acid-base reaction, and compromise the polymerization efficiency of experimental adhesives.²¹ Thus, it may be hypothesized that high amounts of MDP can compromise bonding to dentin in the long term.

A study comparing five adhesives with different MDP concentrations (0 to 15 wt%) showed that the amount of MDP influenced the amount of MDP-Ca salt formed, and this influenced the bond strength to bovine dentin after 30,000 thermal cycles.¹⁸ Another study that evaluated the bond strength and degree of conversion of adhesives containing 0 to 20 wt% of MDP showed that different concentrations of MDP influenced the bond strength, and that experimental adhesive with 10 wt% MDP showed the best combination of bond strength and degree of conversion.¹⁹ Therefore, studies that evaluate the influence of different MDP concentrations on adhesive systems are particularly relevant for both the development of restorative materials and clinical practice.

In this respect, this study aimed to evaluate the influence of different concentrations of MDP (0 wt% to 15 wt%) on microshear bond strength to dentin of the tested experimental adhesives, after storage in distilled water at 37°C for 24 hours and 6 months, when used in etch-and-rinse and self-etching modes. The null hypotheses were that a) the different concentrations of MDP would not influence the dentin bond strength; b) the application mode (etch-and-rinse or self-etching) would not influence the bond strength to dentin; and c) the storage time would not influence the bond strength of the adhesives tested.

Methodology

Five experimental adhesives were evaluated according to their percentage of MDP (0 wt%, 3 wt%, 9 wt%, 12 wt%, and 15 wt%). These adhesives were applied as etch-and-rinse and self-etching systems, except for the adhesive with 0 wt% MDP, which was used only in the etch-and-rinse mode. The tested adhesives and application protocols are described in Table 1.

Table 1. Composition of the experimental adhesives.

Composition (by weight)	Application protocol	
Basic composition consists of: 0.5% CQ, 1% DABE, 0.2% BHT, 10% ethanol, 10% HEMA, 15% TEGDMA, 25% Bis-EMA, 25% UDMA, and 12.85% Bis-GMA.	Etch-and-rinse	Self-etching
MDP% added to the basic composition: 0%, 3%, 9%, 12% or 15%	<ol style="list-style-type: none"> 1. Apply 37% phosphoric acid (Condac 37, FGM, Joinville, SC, Brazil) for 15 s 2. Apply water spray and rinse conditioned areas thoroughly for 10 s 3. Remove rinsing water with absorbent paper, without desiccating dentin 4. Apply two adhesive layers 5. Disperse adhesive and remove solvent with dry air from an air-water syringe for 10 s 6. Light activate for 10 s 	<ol style="list-style-type: none"> 1. Apply two adhesive layers 2. Disperse adhesive and remove solvent with dry air from an air-water syringe for 10 s 3. Light cure for 10 s

HEMA: 2-hydroxyethyl methacrylate; bis-GMA: glycerolate dimethacrylate; DABE: 1,2 diaminobenzene; CQ: camphorquinone; BHT: butylated hydroxytoluene; DPHHP: diphenyliodonium hexafluorophosphate; TEGDMA: triethylene glycol dimethacrylate; Bis-EMA: ethoxylated bisphenol A dimethacrylate; UDMA: urethane dimethacrylate; MDP: 10-methacryloyloxydecyl dihydrogen phosphate.

Ninety extracted caries-free human third molars were used in the study after approval by the Institutional Review Board (CAAE 50831915.6.0000.0093, approval protocol 1.350.250). The crowns were separated from the roots, cut in half in the mesiodistal direction, and each half was embedded in PVC cylinders (1.2 x 2.5 cm) using self-curing acrylic resin (Jet, São Paulo, Brazil), with the exposed flat dentin surface facing up. Smear layers were standardized by wet-sanding dentin surfaces with 600-grit silicon carbide paper (Buehler MetaSerc 250, Lake Bluff, USA) for 1 min under copious water irrigation.

Dentin surfaces were then randomly distributed within the groups, according to the adhesive to be tested (MDP 0 wt%, 3 wt%, 9 wt%, 12 wt%, and 15 wt%), the mode of application (except for the adhesive with 0% MDP, which is not indicated for self-etch application), and storage time (24 hours and 6 months). The adhesive procedures began by delimiting the dentin surfaces with perforated double-sided tape. The adhesives were applied according to the protocols described in Table 1. Light activation was performed with an LED device (Poly Wireless, Kavo, Joinville, Brazil) operating in standard mode with an output irradiance of 1100 mW/cm².

Transparent cylindrical molds 0.7 mm in diameter and 1 mm high (Tygon tubes, R-3603, Saint-Gobain Performance Plastics, Miami Lakes, USA) were positioned on the hybridized dentin surfaces, and the internal volume was filled with composite resin (Filtek Z350 XT, 3M ESPE, St. Paul, USA). The resin cylinders were light activated for 30 s. After 10 min, the molds were removed to expose composite resin cylinders with a bonding area of 0.38 mm². Half of the specimens were stored in distilled water at 37°C for 24 h, whereas the other half were stored in distilled water at 37°C for 6 months.

The μ SBS (n = 10) was evaluated using the wire-loop method, in a universal testing machine (DL2000, EMIC, São José dos Pinhais, Brazil) operating at a crosshead speed of 0.5 mm/min and using a 50 kgf load cell. To this end, the teeth were aligned to allow loading the steel wire-loop (0.2 mm diameter) to be placed as closely as possible to the bonded interface, at the base of the composite resin cylinders. The μ SBS (in MPa) was calculated by dividing the maximum force (in N) by the bonded area (in mm²). Debonded surfaces were examined by a single observer, under a stereomicroscope at 57x magnification (SZX9, Olympus, Tokyo, Japan), to determine the failure mode. Failures were classified as adhesive (at the bonding interface),

cohesive (in dentin or in composite resin) or mixed. The experimental adhesives were also submitted to pH analysis. The pH values were determined using 3 mL of each adhesive, at room temperature (22 to 25°C), using a digital pH meter (PG2000, GEHAKA, São Paulo, Brazil).

The μ SBS data were analyzed by one-way ANOVA separately for 24 h and 6 months to analyze the effect of MDP concentration. These analyses included the MDP 0 wt% groups. In addition, three-way ANOVA was also performed to test MDP concentration (except for MDP 0 wt%), application mode and storage time. All the analyses were followed by applying Tukey's HSD test. The correlation between the MDP concentration of experimental adhesives and bond strength, and between pH and bond strength, were performed using Spearman's rank correlation coefficient. The correlation between pH and MDP concentration was performed using Pearson's correlation coefficient. All analyses were performed with a significance level of 5%.

Results

Microshear bond strength values for the experimental adhesives according to MDP concentration, mode of application and storage time are described in Table 2. The pH values determined for all formulations are also shown in Table 2, and ranged from 3.2 (9 wt% MDP) to 5.2 (0 wt% MDP).

One-way ANOVA indicated significant differences in the adhesives ($p < 0.001$) for both the 24-h and the 6-month time periods. There were no differences regarding the MDP concentrations among the etch-and-rinse groups in the 24-h storage period, or among the self-etch groups in the same period. However, there were significant differences between the etch-and-rinse and the self-etching modes for the same MDP concentration. As for the 6-month storage period, there were no differences in the MDP concentrations among the self-etch groups. However, among the etch-and-rinse groups, 3 wt% MDP showed the highest bond strength value, statistically similar to 9 wt% MDP, but higher than the other MDP concentrations.

Three-way ANOVA indicated statistically significant differences for MDP concentration ($p = 0.006$), application mode ($p < 0.001$) and storage time ($p < 0.001$). All double interactions were statistically significant ($p < 0.05$), except for MDP concentration*application mode ($p = 0.190$). The triple interaction was also significant ($p = 0.010$). As for MDP concentration, the range in bond strength values observed the following order: 9 wt% MDP (9.40 ± 7.50 MPa)^a, 12 wt% MDP (7.89 ± 5.80 MPa)^{ab}, 3 wt% MDP (7.58 ± 6.17 MPa)^{ab}, and 15 wt% MDP (6.37 ± 5.49 MPa)^b. All adhesives used in the etch-and-rinse mode (12.17 ± 6.08 MPa) showed significantly higher bond strength than the adhesives

Table 2. Mean values and standard deviations for the bond strength values according to MDP concentration, application mode and storage time.

MDP concentration	pH	Application mode	Storage time	
			24 h	6 months
0 wt% MDP	5.2	Etch-and-rinse	13.85 (9.40) ^A	6.52 (3.43) ^{BCD}
3 wt% MDP	4.3	Etch-and-rinse	11.55 (7.42) ^{AB}	13.11 (4.60) ^A
		Self-etch	4.40 (2.45) ^{BC}	2.49 (1.20) ^E
9 wt% MDP	3.2	Etch-and-rinse	18.94 (6.27) ^A	9.62 (3.34) ^{AB}
		Self-etch	5.92 (4.84) ^{BC}	2.84 (1.86) ^{DE}
12 wt% MDP	3.3	Etch-and-rinse	15.20 (5.71) ^A	7.33 (2.72) ^{BC}
		Self-etch	5.75 (3.20) ^{BC}	3.81 (2.51) ^{CDE}
15 wt% MDP	3.3	Etch-and-rinse	13.46 (5.21) ^A	7.95 (2.36) ^B
		Self-etch	2.64 (1.50) ^C	1.74 (1.16) ^E

Values followed by the same letter in each column (24 h and 6 months, one-way ANOVA and Tukey's HSD test) are statistically similar ($p > 0.05$).

applied in the self-etching mode (3.75 ± 2.94 MPa). Regarding storage time, the bond strength after 6 months (6.12 ± 4.80 MPa) was significantly lower compared to 24 h (9.47 ± 7.31 MPa). Figure 1 shows the pairwise comparisons among the means of all the groups (Tukey's test following three-way ANOVA).

Figure 2 shows that, the coefficient of determination (R^2) between bond strength and MDP concentration, after the second-degree polynomial, ranged from 0.345 to 0.937. A strong negative correlation between MDP concentration and pH was found for the experimental

adhesives, highlighting Pearson's correlation coefficient of -0.908 and $p = 0.033$ (Figure 3). Correlations between bond strength values (μ SBS) and MDP concentration (% MDP), and between pH and bond strength, for both application modes evaluated, were weak to moderate and non-significant.

The failure mode analysis showed that all groups presented predominantly adhesive (93% to 100%) and mixed (0 to 7%) failures. No group presented a cohesive failure, regardless of MDP concentration, application mode or storage time.

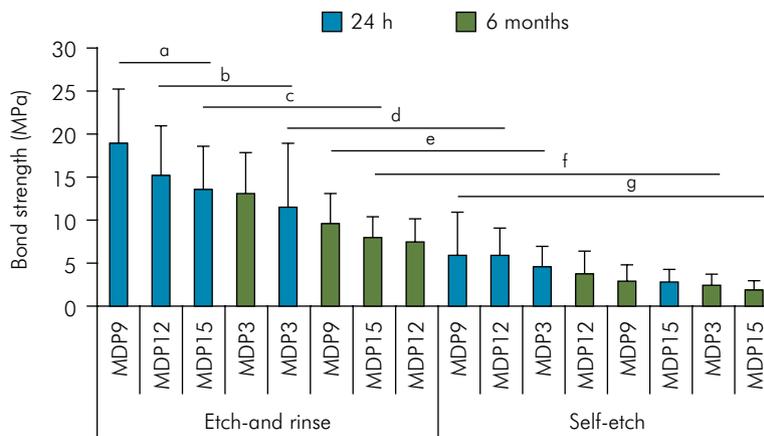


Figure 1. Bar plot showing the μ SBS means and standard deviations for all the groups. Groups sharing the same horizontal line and letter are statistically similar ($p > 0.05$).

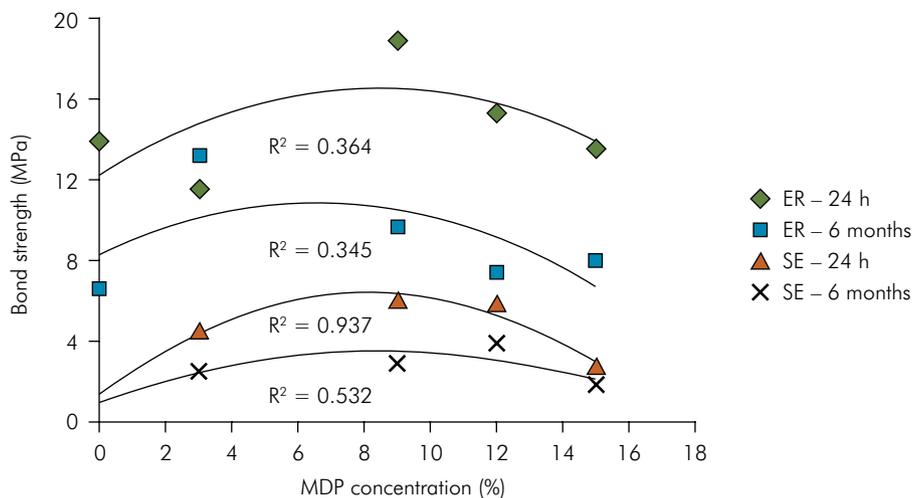


Figure 2. Correlation between bond strength (24 hours and 6 months) and MDP concentration for the experimental adhesives, according to the application mode.

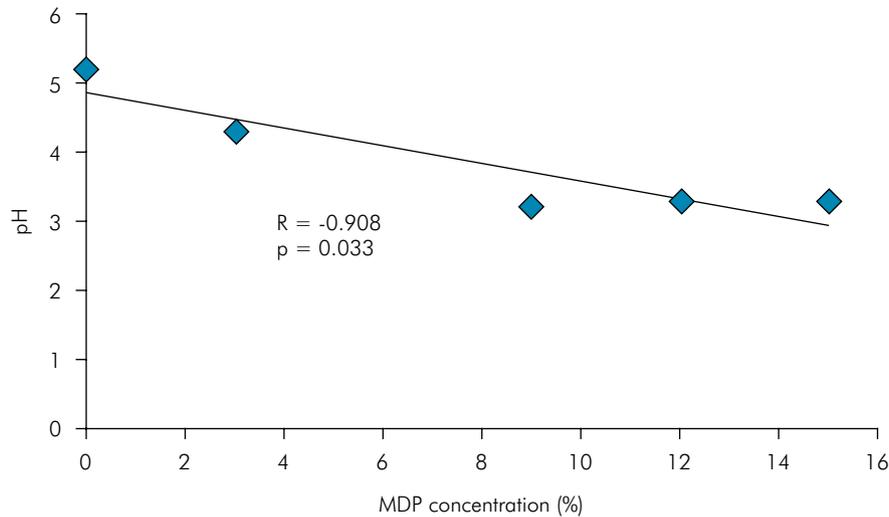


Figure 3. Correlation between pH and MDP concentration for the experimental adhesives.

Discussion

The experimental adhesives, especially 9 wt% MDP, showed the highest bond strength values in both modes of application, indicating that the MDP concentration incorporated into the adhesive may influence bonding to dentin. On the other hand, the bond strength of the 3 wt% MDP adhesive was not significantly affected by storage, and showed only a slight increase. This information confirms the ability of MDP to preserve bonding to dentin from the effects of hydrolysis. This can be attributed to the additional chemical interaction promoted by MDP when bonding with calcium ions to form a strong acid-base zone, which influences bond strength positively.¹⁸ A previous study also tested the range of MDP percentages by weight, between 0 and 20%, in the experimental self-etching adhesives. It showed that formulations with 10% and 15% provided higher bond strength.¹⁹

The differences found in the μ SBS values of the experimental adhesives evaluated may be influenced by other factors, such as the composition of the adhesives. Adhesives may contain different combinations of monomers, concentrations, amounts of water, other solvents and pH levels.^{22,23} However, a specific MDP concentration used in the composition of the experimental adhesives presented in this study could have influenced their bond strength

performance. It can be observed that different MDP concentrations resulted in different bond strength values, suggesting that there may be an “ideal” concentration of MDP that is more appropriate for a specific composition.

The composition used for the experimental adhesives in this study may differ significantly from that of the commercially available adhesives. The composition of the commercial adhesives, regarding components and percentages used, is not entirely disclosed by the manufacturers, making it difficult to make comparisons between commercial and experimental adhesives. Because MDP has an acidic monomer, chemical bonding with the dental structure may occur. This is because the MDP monomer bonds with the Ca^{2+} ions deposited under the collagen layer or in the hybrid layer in the self-etching approach, to form the MDP-Ca salt.^{5,24,25} In fact, the results of the present study show that the amount of MDP is important not only for bonding, but also for hydrolytic stability.

The present study observed that the etch-and-rinse mode of application showed higher bond strength values than the self-etching mode, regardless of MDP concentration. The pH analyses demonstrate that the experimental adhesives used in this study were ultra-mild despite the amount of MDP. Except for the 3 wt% MDP adhesive (pH 4.3), all the other adhesives showed pH 3.2 to 3.3. This may explain why the etch-and-rinse mode showed better results. It was also

observed that the etch-and-rinse approach used with an ultra-mild MDP-based universal adhesive (pH 3.1) improved the bonding to dentin, compared with the self-etch mode.¹⁴ Hence, the adhesives evaluated in the present study were found to be better suited for use with an etch-and-rinse approach, despite of the amount of MDP. This result is in agreement with a recently published systematic review.¹³ Several types of functional monomers have been used in different self-etching and universal adhesive systems. Universal adhesives can be used with self-etch, selective-etch and total-etch bonding systems. The composition of the present experimental adhesive can be understood as being that of a universal adhesive system, which includes a functional monomer (MDP), and can be used with both strategies. The results of this study also indicate that the experimental adhesive used behaved like a universal adhesive, since relatively high bond strengths were observed for both application modes, even after six months of water storage. The function of MDP is not completely clear when universal adhesives are used in an etch-and-rinse mode. However, it has been previously reported that this monomer may interact chemically with collagen.²⁶

Use of 37% phosphoric acid in dentin for 15 s in self-etching adhesive systems is not indicated. The use of acid as a separate step has the purpose of demineralizing the hydroxyapatite, and opening space in the dentinal tubules for penetration of the adhesive monomers and exposure of the collagen web to form the hybrid layer. However, this formation occurs more frequently with self-etching adhesives, owing to their more hydrophilic structure, because a greater amount of water forms a more permeable and less resistant hybrid layer.^{24,25}

On the one hand, a study analyzing the bond strength and penetration of three adhesive systems, with and without acid etching, after 24 hours and 5000 thermal cycles, concluded that acid etching improved dentin penetration, without interfering in

the bond strength.⁴ On the other hand, another study evaluated three commercial adhesives with MDP in their composition, in etch-and-rinse and self-etching modes of application. It showed that the acid etching of the etch-and-rinse system enabled the formation and penetration of a hybrid layer, and a more efficient and thicker acid resistant zone than that formed by the self-etching adhesive system.²³

The data shown in Table 2 and Figure 1 indicate that the experimental adhesives did not show good performance for the bond strength test in the self-etching mode. The pH values of the formulations evaluated in the present study indicated that the acids in the self-etching systems were weak. The literature reports that self-etching adhesives usually have a pH of about 2, which is enough to act on the hybrid layer efficiently and allow incorporation of the monomers.^{1,27}

Conclusions

It can be concluded that MDP concentration and application mode influenced the bond strength of the experimental adhesive systems evaluated. The formulations with low concentration of MDP (up to 9 wt%) showed better results for bond strength and bond strength degradation over time. No significant correlations were observed between bond strength and MDP concentration, or between pH and bond strength, for neither of the application modes evaluated. A strong negative correlation between MDP concentration and pH was found for the experimental adhesives. Regarding the application mode, the etch-and-rinse approach presented higher bond strength values for the tested compositions than the self-etching application mode.

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