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Evaluation of pH, ultimate tensile strength, and micro-shear bond strength of two self-adhesive resin cements

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Abstract: The aim of this study was to evaluate the pH, ultimate tensile strength (UTS), and micro-shear bond strength (µSBS) of two self-adhesive resin cements to enamel and dentin. Sound bovine incisors (n = 10) and two self-adhesive resin cements (*i.e.*, RelyX U-100 and seT PP) were used. The pH of the resin cements was measured using a pH-indicator paper (n = 3). Specimens for UTS were obtained from an hourglass-shaped mold. For µSBS, cylinders with internal diameter of 0.75 mm and height of 0.5 mm were bonded to the flat enamel and dentin surfaces. Bonded cylinders were tested in the shear mode using a loop wire. The fracture mode was also evaluated. The cement seT PP showed a low pH; U-100 showed significantly higher UTS (49.9 ± 2.0) than seT PP (40.0 ± 2.1) ($p < 0.05$) and high µSBS to enamel (10.7 ± 3.7). The lowest µSBS was found for seT PP to dentin (0.7 ± 0.6); seT PP to enamel (4.8 ± 1.7), and for U-100 to dentin (7.2 ± 1.9), showing an intermediate µSBS value ($p < 0.05$). Adhesive failure was the most frequently observed failure mode. The resin cement that presented the lowest pH and UTS also presented the lowest micro-shear bond strength to enamel and dentin.

Keywords: Resin Cements; Shear Strength; Dental Enamel; Dentin; Hydrogen-Ion Concentration.

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Introduction

Resin cements have provided great advances for both direct and indirect procedures because of their ability to bond to both dental structures and prosthodontics materials. Traditional resin cements can be divided into two subgroups according to the adhesive system used to prepare the tooth prior to cementation. One group utilizes etch-and-rinse adhesive systems (two- or three-step), whereas for the other group, dental substrates are prepared using self-etch primers/adhesives (one- and two-step).[1]

Traditional resin cement bonding has been reported to be erratic because it relies on the sensitivity of the required adhesive.[2,3] In 2002, a new category of resin cements was introduced to dentistry. User-friendly, self-adhesive resin cements were designed to bond to dental tissues without the need for any adhesive system or conditioner.[1,4,5]

It has been reported that self-adhesive resin cements provide bond strengths to dentin,[6,7] glass ceramics,[8] or zirconia,[9] which are equivalent to those of conventional resin cement systems.

The composition of self-adhesive cements is based on the presence of methacrylate carboxylic or phosphoric[10] monomers that demineralize/infiltrate into the tooth substrate, resulting in micro-mechanical retention.[6,7] It has been reported that chemical retention may also occur by monomer bonding to Ca^{2+} ions derived from hydroxyapatite.[11]

The ability of self-adhesive resin cements to self-adhere to the dental tissues is based on their intrinsic acidity.[10] The pH has to be low enough to promote tissue demineralization.[12] Low pH, however, has been associated with lower mechanical properties, and reduced mechanical properties of the cement may result in reduced bond strengths.[5] Reduced tensile bond strengths to dentin have been correlated with reduced mechanical properties of composite resins.[13] If this principle applies to resin cements as well, one should expect lower bond strengths from resin cements that present lower mechanical properties.

Most studies have used either the microtensile or the traditional shear bond strength methods to evaluate resin cement bonding to dental substrates.[14,15,16,17,18] However, these tests have some limitations due to the increased rate of cohesive failures of the substrates and non-uniform stress distribution.[17,19,20]

Therefore, the aim of this study was to evaluate the pH, UTS and micro-shear bond strength to enamel and dentin of two self-adhesive cements.

The null hypothesis was that lower pH and UTS would not be associated with lower bond strengths of the self-adhesive cements to enamel and dentin.

Methodology

The following two self-adhesive resin cements were used: RelyX U-100 (3M/ESPE, St. Paul, USA) and seT PP (SDI, Bayswater, Australia). Cement compositions are presented in Table 1.

The resin cements were manipulated for 20 s, spread on pH indicator strips (Merck Millipore, Darmstadt, Germany), and polymerized for 20 s at 600 mW/cm^2 (Optilux 501, SDS Kerr, Danbury, USA). After 40 s, the resultant color change was compared with the scale provided by the manufacturer. Two operators performed this procedure three times for each cement (n = 3).

Ultimate Tensile Strength (UTS)

An hourglass-shaped rubber matrix, 10-mm long and 2-mm wide at the neck and 1-mm deep (Odeme, Joaçaba, Brazil), was used to prepare the resin cement specimens. After lubricating the matrix with a thin film of petroleum jelly to facilitate specimen removal, the cements were manipulated for 20 s and inserted into the matrix with the aid of a Centrix syringe (DFL, Rio de Janeiro, Brazil). A plastic matrix strip was placed on the cement and the surface was polymerized for 20 s at 600 mW/cm^2. Ten specimens were prepared for each resin cement (n = 10). The specimens were stressed to failure by applying tension using an Instron 3342 (Instron, Canton, USA) universal testing machine at a crosshead speed of 0.5 mm/min.

Micro-shear bond strength

The micro-shear bond strength to enamel and dentin was tested on the same tooth. First, the enamel surface was exposed, bonded, and tested. Then, the surface was further abraded to expose dentin for bonding and testing.

Twenty sound bovine incisors were selected (n = 10). After cleaning, the teeth were sectioned at the cement-enamel junction using a diamond disc (7016 KG Sorensen, Barueri, Brazil) and the roots were discarded.

Table 1. Manufacturer, composition, and application mode of the self-adhesive resin luting cements used in this study.

Material	Manufacturer	Composition	Application Technique
RelyX U-100	3M/ESPE (426343)	Base: glass fiber, methacrylate phosphoric acid esters, dimethacrylates, silanated silica, sodium persulfate. Catalyst: glass fiber, dimethacrylates, silanated silica, p-toluene sodium sulfate, calcium hydroxide.	1. Mix cement (20 s) 2. Apply mixture 3. Light activation (20 s)
seT PP	SDI (S1101113)	Methacrylate ester phosphoric acids, UDMA, photoinitiator, fluoride aluminum silicate glass and pyrogenic silica.	1. Mix cement (20 s) 2. Apply mixture 3. Light activation (20 s)

Measurement of the pH of cements.

Crown fragments were embedded in transparent acrylic resin (JET, São Paulo, Brazil) and the buccal surfaces were abraded using a polishing machine with 120-grit silicon carbide (SiC) abrasive papers (Aropol E, Arotec, São Paulo, Brazil) under water cooling until the enamel was flattened. Subsequently, 600-grit SiC abrasive papers were used for additional 60 s to standardize the smear layer.

Transparent Tygon tubes (TYG-030, Saint-Gobain Performance Plastic, Miami Lakes, USA) with an internal diameter of 0.75 mm and height of 0.5 mm were positioned and held in place on the surface of each tooth with the help of pliers. Four Tygon tubes were bonded onto each bovine crown.

All cements were manipulated for 20 s and inserted into the Tygon tube using an exploratory probe; then, a polyester matrix was placed on the Tygon tube to ensure a smooth and uniform surface. After removing lateral excess, the inserted cement was light activated for 20 s at 600 mW/cm^2.

The bonded sets were stored in water at 37°C for 24 h. Thereafter, the tubes were carefully removed with a blade, and the resin cement cylinders were checked with a light stereomicroscope (10×) to discard any specimens with air bubbles or evident defects at the interface. No such specimens were observed and all were deemed testable. The flash of resin cement below the tube rim was also removed with a blade.

An Instron 3342 (Instron, Canton, USA) universal testing machine was used for the micro-shear bond test. The embedded tooth crown, containing four bonded resin cement cylinders, was attached to a testing device and adapted to the universal testing machine. A thin wire (Morelli Ortodontia, São Paulo, Brazil) with a diameter of 0.2 mm was looped around the resin cement cylinder and gently held against the bonded interface. A shear force was applied to each specimen at a crosshead speed of 0.5 mm/min until failure occurred. The force required to produce failure was then divided by the bonded area of the resin cement cylinder, and the bond strength values were expressed in MPa.

After all the tests on enamel were completed, the same embedded crowns were further abraded to remove the enamel and expose the dentin surfaces, which were polished as described above and bonded according to the same protocol used for the enamel. Four cement cylinders were bonded to each surface and tested accordingly. For this analysis, the four values obtained from each tooth were averaged and the means were used for the calculations.

Failure mode evaluation

The fractured surface of each resin cylinder was evaluated under a stereoscope (Kozo Optical and Electronical Instrumental, Nanjing, China) at 40× magnification. Failures were classified as adhesive, cohesive in cement, and mixed.

Failures were adhesive when no residual cement material could be observed on the tooth surface; cohesive in cement when residues of the cement covered the tooth surface over the entire diameter of the bonded area; and mixed when the cement residue partially covered the bonded area.

Statistical analysis

Statistical analysis was performed using the SigmaPlot 12 software (SigmaPlot v. 12.3, Systat Software Inc., San Jose, USA). All data were analyzed for normality of distribution using the Kolmogorov–Smirnov test ($\alpha = 0.05$). The ultimate tensile strength (UTS) data were tested by one-way analysis of variance and Tukey's tests ($\alpha = 0.05$). The normality was violated for data from µSBS, and the data set was analyzed using the Kruskal-Wallis and Student-Newman-Keul's multiple comparison procedures.

Results

The pH interval was between 4.4-4.7 for U-100, and between 3.6-3.9 for seT PP. The UTS was significantly higher for U-100 (49.9 ± 2.0) than for seT PP (40.0 ± 2.1) ($p < 0.05$) (Table 2).

The micro-shear bond strength values showed statistical significance: U-100 cement presented the highest bond strength values to enamel (10.7 ± 3.7); the bond strength values of U-100 cement to dentin (7.2 ± 1.9) were similar to those of seT PP for cement to enamel (4.8 ± 1.7); and the lowest bond strength values to dentin (0.7 ± 0.6) were found for seT PP.

The type of failure most frequently found for both materials was adhesive, irrespective of the type of substrate. The distribution of failure modes (%) among the treatments is shown in Figure 1.

Discussion

The results of this study required the rejection of the null hypothesis because the cement with the lowest pH and UTS also presented the lowest bond strength values.

In the present study, the micro-shear bond strength of two self-adhesive resin cements to bovine dentin and enamel was evaluated. To avoid any influence on the cement bond strength to the substrates, no restorative material was used. Several studies have evaluated the bond strength of cements to dentin using the μ-tensile test.[14,15] In this study, the μ-shear test was chosen because of the significant advantage it has over the μ-tensile methods, as μ-shear is pre-stressed prior to testing only by Tygon mold removal.[20]

Evaluation of bond strength to enamel using the μ-tensile test is problematic because the cutting procedure to obtain the beams produces defects on the corners of the sticks, resulting in high levels of defects that compromise testing.[19] Another advantage of our approach is the possibility of using the same tooth to evaluate the bond strength to both the enamel and dentin.

To interpret the bond strength results, the pH of the resin cements was analyzed. The interface produced by self-etch adhesives largely depends on the manner in which their functional monomers interact with the dental substrate.[6] In part, the depth of interaction of self-etch cements with enamel and dentin depends on the pH of the cement.[12] Therefore, the pH value of the cement plays a crucial role: it has to be acidic enough to guarantee proper demineralization of both enamel and dentin, but it should not be too acidic in order to avoid excessive hydrophilicity.[10] The hydrophilic of the cement and the low pH in the polymerized material, may be one of the reasons that could compromise the mechanical stability by excessive water sorption.[5,21] In this study, the seT PP cement was more acidic than the U-100 cement (Table 2).

The tested cements appear to contain the same acidic monomer, *i.e.*, phosphoric acid methacrylate.

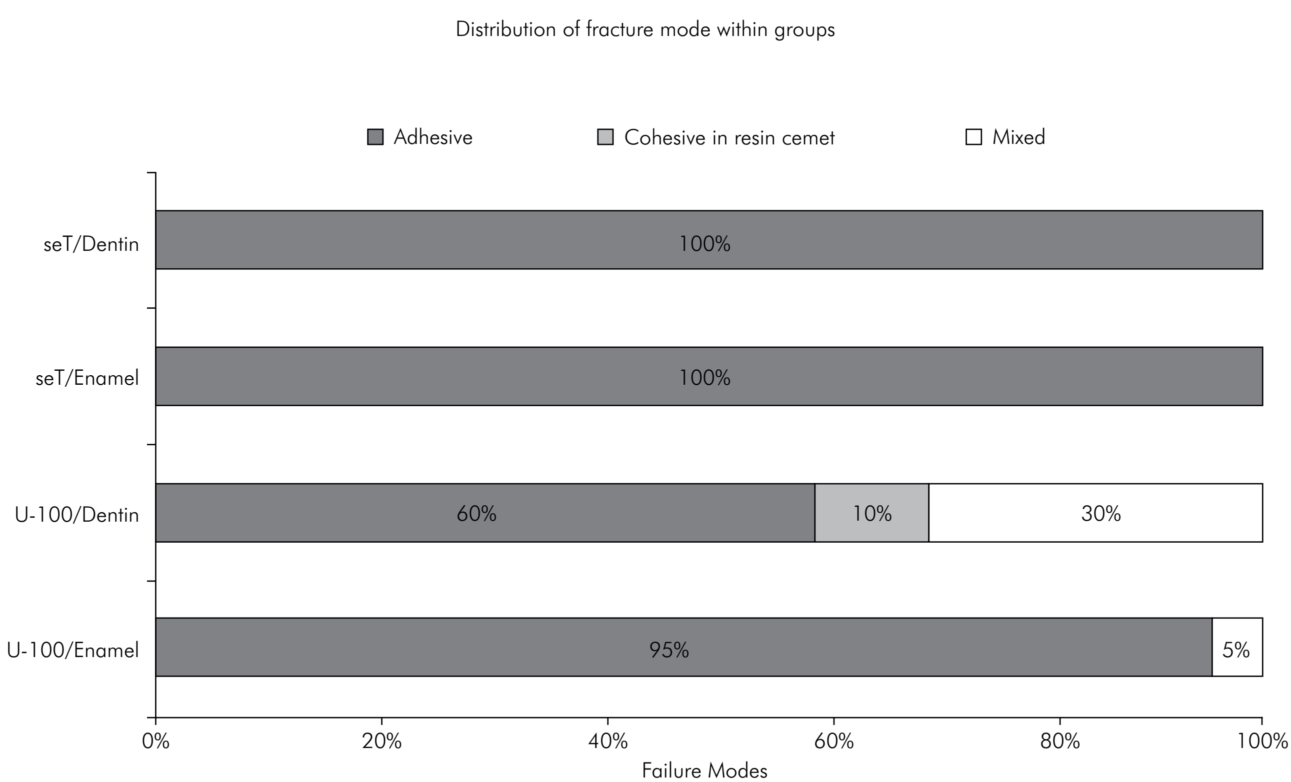

Figure 1. Incidence of failure modes (%) of self-adhesive resin cements, RelyX U-100 and seT PP to dentin and enamel, analyzed by stereomicroscope.

Table 2. Ultimate tensile strength (UTS), micro-shear bond strength (MPa) and pH values of the materials used in this study, and percentage of premature failures from each experimental condition (%).*

Resin Cement	UTS	Substrate μSBS	
		Enamel	Dentin
RelyX U-100 (pH = 4.4-4.7)	49.9 ± 2.0^A	10.7 ± 3.7^a (17.5%)	7.2 ± 1.9^b (10%)
seT PP (pH = 3.6-3.9)	40.0 ± 2.1^B	4.8 ± 1.7^b (32.5%)	0.7 ± 0.6^c (57,5%)

**UTS* column: different capital letter indicates statistically significant differences ($p < 0.05$).
*μSBS column: groups with different superscript letters are statistically significant ($p < 0.05$).

However, U-100 cement contains calcium hydroxide, which reacts with the remaining acidic monomers and improves the neutralization of the polymerized cement. This might explain the higher UTS values of U-100 cement compared with that of seT PP (Table 2) because pH neutralization affects the mechanical properties of the material.[10]

Another possible explanation for the lower UTS shown by seT PP is the presence of the monomer UDMA, which has high flexibility, low flexural resistance, and low impact strength due to the presence of weak hydrogen bonds (urethane-hydroxyl N-H interactions).[22]

The lower bond strength for seT PP could also be explained by the fact that in the initial phase, low pH is important to hybridize the dental substrate but it is not desirable after the cement has been mixed. If the cement continues to present a low pH, this may compromise the hybrid layer.[23] On the other hand, the presence of calcium hydroxide in the U-100 cement neutralizes the pH at the adhesive interface.[23]

Viotti *et al.*[15] found that among the nine resin cements tested, seT PP had the lowest bond strength values. In another study, this cement showed the lowest initial bond strengths when used on dentin; after 1 year, no specimens could be tested because they had debonded prematurely.[24] Nevertheless, in this study, the bond strength results observed for seT PP cement to enamel showed values close to those found in another study.[25] The large number of premature failures found for seT PP in this study might indicate the incapability to achieve a cement bond with the tooth (Table 2).

In general, the bond strength values observed in this study were low, and they were lower to dentin than to enamel. This might be attributable to the conditions under which cement specimens are produced for micro-shear testing. When the cement is applied with an exploratory probe, no pressure is exerted on the cement on insertion into the matrix. According to Goracci *et al.*,[26] the high viscosity of this material makes it difficult for it to penetrate into the dentin, a characteristic that may be overcome by exerting pressure during the cementation process. Moreover, when the cement was applied under pressure, there was evidence of reduced porosity at the interface.[6]

On the other hand, micro-mechanical interlocking of the adhesive resin with the enamel surface depends more on the surface receptiveness.[27] In the present study, abrasion was performed on enamel using SiC600 for 60 s, and this method apparently improved the micro-mechanical interlocking and, probably, provided greater opportunity for the adhesive resin to chemically interact with hydroxyapatite.[6,7,11] In a recent review article, Ferracane *et al.*[5] showed that many resin cements present better bond strength to enamel than to dentin.

Self-adhesive resin cements do not require pre-treatment of the tooth structure. Additional advantages of these products are the decrease in or elimination of post-operative sensitivity and lower susceptibility to moisture.[2,3] There are various self-adhesive cements in the market, with different compositions and characteristics. These differences may lead to *in vivo* variations in the long-term clinical success of luting restorations.[10] Although lower bond strengths are usually expected when using a self-adhesive resin cement, improved bond strengths might be achieved by prior application of phosphoric acid to enamel and dentin.[18] Although this might improve bond strength, one could argue that it defeats the principle of self-adhesiveness and the user-friendliness of such materials.

Conclusion

The U-100 self-adhesive cement showed high bond strengths to both bovine enamel and dentin compared with seT PP self-adhesive cement. The low pH of the resin cement may compromise the UTS and does not guarantee high bond strength.

Acknowledgments

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