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Microtensile Bond Strength of Methacrylate and Silorane Resins to Enamel and Dentin

Gisele Rodrigues da Silva[1], Isabela Sousa Araújo[2], Rodrigo Dantas Pereira[1], Bruno de Castro Ferreira Barreto[1], Célio Jesus do Prado[2], Carlos José Soares[1], Luís Roberto Marcondes Martins[3]

[1]Department of Operative Dentistry and Dental Materials, School of Dentistry, UFU - Federal University of Uberlândia, Uberlândia, MG, Brazil
[2]Department of Occlusion, Fixed Prosthodontics and Dental Materials, School of Dentistry, UFU - Federal University of Uberlândia, Uberlândia, MG, Brazil
[3]Department of Operative Dentistry, Piracicaba School of Dentistry, UNICAMP - University of Campinas, Piracicaba, SP, Brazil

Correspondence: Dra. Gisele Rodrigues da Silva, Avenida Pará, 1720, Bloco 4L, Anexo A, Sala 4LA33, Campus Umuarama, 38400-902 Uberlândia, MG, Brasil. Tel: +55-34-3218-2255. e-mail: giselerosilva@yahoo.com.br

The aim of this study was to evaluate the microtensile bond strength (μTBS) of two substrates (enamel and dentin) considering two study factors: type of composite resin [methacrylate-based (Filtek Supreme) or silorane-based (Filtek LS)] and aging time (24 h or 3 months). Twenty human molars were selected and divided into 2 groups (n=10) considering two dental substrates, enamel or dentin. The enamel and dentin of each tooth was divided into two halves separated by a glass plate. Each tooth was restored using both tested composite resins following the manufacturer's instructions. The samples were sectioned, producing 4 sticks for each composite resin. Half of them were tested after 24 h and half after 3 months. μTBS testing was carried out at 0.05 mm/s. Data were analyzed by three-way ANOVA and Tukey's HSD tests at α=0.05. Significant differences between composite resins and substrates were found ($p<0.05$), but no statistically significant difference was found for aging time and interactions among study factors. The methacrylate-based resin showed higher μTBS than the silorane-based resin. The μTBS for enamel was significantly higher than for dentin, irrespective of the composite resin and storage time. Three months of storage was not sufficient time to cause degradation of the bonding interaction of either of the composite resins to enamel and dentin.

Key Words: microtensile bond strength, BisGMA methacrylate composite resin, silorane composite resins, enamel, dentin.

Introduction

Resin composites have been widely used in direct adhesive restorations (1,2) due to their excellent physical and mechanical properties (3). However, these composites have inherent shortcomings that are mainly relative to polymerization shrinkage (4). Shrinkage creates stress and compromises restoration integrity (3), which leads to microleakage (1) and failures in the tooth-restoration interface (5,6). Some restorative strategies have been developed in order to decrease the polymerization shrinkage and its effects, such as the incremental filling technique (2,4,5), curing light intensity (1) and photoactivation time (3). Additionally, the manufacturers have worked to improve resin composition by increasing the volume and size of inorganic fillers and developing new monomers (4-6).

New types of monomers, known as low-shrinkage monomers, have been developed with the intention of reducing problems inherent to resins based on methacrylates (6), like monomeric volume reduction during polymerization shrinkage (4,5). Silorane composite resin is filled with a combination of fine quartz particles and radiopaque yttrium fluoride. The quartz surface is modified with a silane layer (7). Silorane technology has afforded a highly hydrophobic restorative material with lower polymerization shrinkage that results in lower residual shrinkage stress (2,4,5). This composite resin presents also better color stability as well as lower insolubility in biologic fluids and adequate physical and mechanical properties, making it clinically suitable (7,8). Studies confirm that a commercial silorane-based composite accounts for less than 1.0% of total volumetric shrinkage, compared with 2.0–3.5% for BisGMA-based composites and causes less tooth deflection (2,4,5) and microleakage (6). Some studies have shown that this low shrinkage of composites provide clinical longevity (9,10).

Composite resin bonding strength to dental substrate varies with the substrate. Tooth structure consists mostly of dentin (11), which is a hard tissue containing approximately 45% mineral, 35% of organic matrix and 20% water, by volume. Dentinal tubules extend radially from the pulp through the dentin and toward the dentin-enamel junction (12). Enamel is a highly mineralized tissue, which covers the entire crown of the tooth and consists of 92-96% of inorganic matrix, 1-2% organic material and 3-4% of water by weight (13). Thus, the physicochemical characteristics of these substrates probably influence the quality of the composite resin adhesion. More studies that make simultaneous comparisons between different resin monomers and tooth structures, concerning microtensile bond strength (μTBS), would be of great value.

Moreover, storing samples to simulate the aging in the oral environment is an important method for monitoring the survival of restorative materials (14). However, the

literature shows that laboratory storage and actual aging do not occur in exactly the same way since oral environment is complex and composed by several interrelated factors such as temperature, pressure, chemical and mechanical phenomena, among others. Nevertheless, artificial aging is important for monitoring restoration, improving the correlation of the *in vitro* results with clinical outcomes (14).

The aim of this study was to test the effect of the composite resin composition and aging time on the μTBS to different dental substrates. The null hypothesis is that the composite resin composition and the aging time have no effect on μTBS to enamel or dentin substrates.

Material and Methods

After approval from the Federal University of Uberlândia Ethics Committee (CEP / UFU 001/10), 20 intact third molars extracted for orthodontic reasons were collected. The teeth were stored in an aqueous 0.2% thymol solution for no more than 3 months, cleaned with periodontal curettes and pumice prophylaxis and then maintained in distilled water at 4 °C.

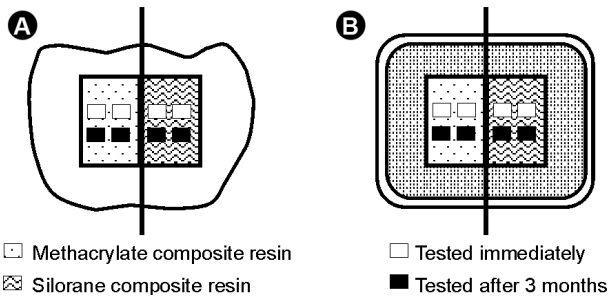

Figure 1. Schematic illustration describing the study design and specimen preparation. A: Restorations on enamel: buccal surface of the tooth. B: Restorations on dentin: occlusal surface of the tooth.

To test the μTBS to dentin, the tooth roots (n=10) were embedded in polyester resin (Aerojet, São Paulo, SP, Brazil) inside a silicone matrix (Aerojet) and their coronal occlusal surfaces were ground wet onto 320- to 600-grit silicon carbide paper. Abrasion continued until the superficial dentin was completely exposed, which was confirmed by surface analysis with a stereomicroscope (Leica, Weztlar, Hesse, Germany). To test the μTBS to enamel, the buccal enamel surface (n=10) was abraded with 600-grit silicon carbide paper for 30 s until the surface was flattened.

The substrates were separated in the middle by a cover slip and restored with both resins simultaneously (Fig. 1). The substrate was restored using both resins to exclude the influence of possible morphological differences of the specimens caused by intrinsic mineralization. Half of specimens were restored with the methacrylate-based resin (Filtek Supreme A2, 3M ESPE) (FSU) after application of a two-step self-etching adhesive system (Clearfil SE Bond, Kuraray, Okayama, Japan), and half with the silorane-based composite (Filtek LS A2, 3M ESPE, St. Paul, MN, USA) (FLS) after application of its specific adhesive system. All procedures were done following the manufacturers' protocol (Table 1). Two 2-mm-thick increments were used on enamel and dentin to build composite resin restorations measuring 4x4x4 mm (4). Photoactivation was performed with a halogen light source (Demetron 501, 550 mW/cm^2, Kerr, Orange, CA, USA) for 40 s each increment.

The restored teeth were stored for 24 h at 37 °C and then cut into sticks with 1 mm^2 cross section area using a precision saw (Isomet 2000, Buehler, Lake Bluff, IL, USA) with speed of 300 rpm. Four sticks were obtained for each

Table 1. Materials, compositions, manufacturers and protocols of usage

Material	Composition	Application instructions
Clearfil SE Bond Adhesive System	Primer: HEMA, 10MDP, DMA hydrophilic, 12-MDBP, water Bond: HEMA, 10MDP, BisGMA , N,N-diethanol-p-toluidina, DMA hydrophilic, camphorquinone, silanized colloidal silica.	1. Application of primer: 20 s; 2. Mild air-drying 3. Bond application 4. Photoactivation for 10 s.
Silorane Adhesive System	Self-etching primer: phosphorylated methacrylates, vitrebond copolymer, BisGMA, HEMA, water, ethanol, silane-treated silica filler, initiators, stabilizers. LS Bond: Hydrophobic methacrylates, phosphorylated methacrylates, TEGM), silane-treated silica filler, initiators, stabilizers.	1. Application of one layer of self-etching primer during 15 s with mild air-drying, followed by photoactivation for 10 s; 2. Application one layer, removal of excess and photoactivation for 10 s.
Filtek Supreme resin	Matrix: methacrylate resin , BisGMA, BisEMA, UDMA, initiator system: camphorquinone, stabilizers and pigments. Filler: Silanized zirconia,	Application of two 2-mm-thick layers and photoactivation of each layer for 20 s.
Filtek LS resin	Matrix: 3,4 epoxycyclohexylethyl cyclopolymethylsiloxane, bis-3,4-epoxycyclohexylethylphenylmethylsilane. Filler: Silanized quartz; yttrium fluoride 76 wt%	Application of two 2-mm-thick layers and photoactivation of each layer for 20 s.

Manufacturer information.

longitudinal restoration. Half the sticks were used for the immediate test and the other half were tested after 3 months of storage in water at 37 °C.

The area of bond interface of each stick was individually measured with a digital caliper (Starrett 727-2001, Itu, SP, Brazil). The specimens were actively gripped onto a Geraldeli's device (15) with cyanoacrylate adhesive (Superglue Gel, Loctite, Henkel Corp., Avon, OH, USA). Each testing assembly was connected to a universal testing machine (EMIC, São Jose dos Pinhais, PR, Brazil) and the specimens were stressed to failure under tensile force at 0.5 mm/min (15). Final values were expressed in MPa considering the bonded area. The μTBS of each sample was defined as the average of results from two sticks, and assuming the tooth as the experimental unit (16). All tested sticks were checked on the stereomicroscope (Leica) to ensure that the failure occurred at the adhesive interface. Two sticks that had cohesive failure and different failures of the adhesive were excluded from the study.

The Shapiro-Wilk and Levene tests were conducted to test the data for normality and homogeneity. Data were transformed using $\log_{10}$ to fulfill this requirement and three-way ANOVA was used, followed by post hoc Tukey's HSD (Honestly Significant Difference) to determine whether there was a significant difference in the bond strength (α=0.05). For all analyses was used SigmaPlot V 12.0 software (Systat Software, Inc., San Jose, CA, USA).

Results

The μTBS results are presented in Table 2. The statistical analysis showed a significant effect for composite resin ($p<0.001$) and for dental substrates ($p<0.001$). However no significant effect was found for aging time ($p=0.329$), for interactions between composite resin and aging time ($p=0.083$), composite resin and dental substrate ($p=0.424$), dental substrate and aging time ($p=0.622$), or for the interaction among all three study factors ($p=0.437$). Tukey's HSD test showed that μTBS on enamel was higher than on dentin, for all composite resins and aging times. The methacrylate-based composite resin had higher μTBS values than silorane-based ones, irrespective of dental substrate or aging time ($p<0.001$).

Table 2. Microtensile bond strength of methacrylate and silorane-based resin composites on the dental substrates, enamel and dentin, according aging time.

Substrate	Immediately		3 months	
	Filtek Supreme	Filtek LS	Filtek Supreme	Filtek LS
Enamel	35.1±10.1 ^{Aa}	16.7±2.9 ^{Ab}	36.1±6.8 ^{Aa}	13.6±1.94 ^{Ab}
Dentin	26.3±6.8 ^{Ba}	10.9±2.5 ^{Bb}	27.1±7.2 ^{Ba}	10.1±1.8 ^{Bb}
Pool average	22.3±11.2$^{\beta}$		21.7±11.7$^{\beta}$	

Different letters indicate statistically significant difference: capital letters for comparison between dental substrates (in columns) and lowercase letters for comparison between composite resins within each storage time (in rows) ($p<0.05$). The Greek letters indicate comparison between storage times.

Discussion

The null hypothesis was rejected. Methacrylate resin showed higher bond strength than silorane regardless of dental substrate and aging time. Additionally, the μTBS on enamel was higher than dentin regardless the composite resin type and aging time. On the other hand, the storage time had no effect on μTBS results.

Although the silorane system is based on cationic polymerization, which occurs by photo cationic ring opening and results in lower polymerization shrinkage compared with methacrylate-based resins (5,17), silorane had lower μTBS values on both substrates. It is important to observe that the low polymerization shrinkage of a composite does not always indicates reduction of the shrinkage stress on the restored tooth (2,5). The silorane-based resin forms a low-viscosity layer and may induce shrinkage stress similar to that produced by methacrylate resins (17). The viscoelastic behavior changes that occur during the polymerization of predominantly elastic-viscous material can make the development of strains an event of significantly complex polymerization. The low initial flow presented by the base resin can restrict the flow of viscoelastic silorane, increasing the stress despite the low shrinkage (17). However, it is worth emphasizing that the polymerization stress is a physical condition that is not solely based on material properties but also on the geometry of the cavity and the boundary conditions (2,5). The other aspect that may explain the results of the present study was the need of using a dedicated adhesive system for the silorane composite resin (18). However, both adhesive systems were two-step self-etching adhesives to avoid the influence of this factor. Clearfil SE Bond was used in combination with Filtek Supreme because it is considered as the "gold standard" (19) for this class of adhesive systems. The primer agent of the silorane restorative system presents different curing method from Clearfil SE Bond.

The silorane primer agent is first light-cured and then the bonding agent is applied. Therefore, the primer agent creates the hybrid layer, in contrast with the conventional self-etching adhesive systems, where the hybrid layer formation is determined by the combination of primer and bonding agent. The silorane adhesive system produces an interface composed by a hybrid layer, produced by the primer agent, an intermediate resin layer with

low viscosity and finally the composite resin. Due to this complex process, a weak bonding interaction between the two substrates may compromise the μTBS (18). Moreover, the pH of the silorane-based self-ethcing primer is less acidic than the methacrylate-based adhesive used in this study (20). The primer agent of the silorane composite resin is cured before application of the bond; therefore the dentin hybridization may be entirely dependent on the degree of demineralization, penetration, and cross-linking produced by the primer (18). pH and the resulting hydrophilicity of the silorane primer may greatly determine the extent of resin permeation into dentin and enamel (21). Although this *in vitro* test showed a significant difference between both composite resins, a one year clinical study that analyzed the performance of Class I and II cavities of three different composite resins, the silorane-based system showed acceptable results (9). The restorations had no advantage over those with methacrylate-based composite combined with etch-and-rinse adhesive. However, silorane restorations tended to degrade in terms of marginal adaptation compared with baseline values. In their two-year follow-up, the three restorative systems showed statistically similar clinical performances (9).

Bond strength of the composites did not differ whether immediately after or three months after manufacture. This was likely because the time interval was insufficient to reduce the strength of the adhesive resins. For example, Martins et al. (22) found that the properties of the adhesive layer start to degrade after 6 months of storage. Dental substrate was another studied factor and it was observed that μTBS on enamel was greater than on dentin. The self-etching adhesives essentially modify the smear layer and provide chemical adhesion to the mineralized component of enamel (23). The effectiveness of some self-etching adhesive on enamel is probably due to a secondary connection caused by calcium affinity (24). Nevertheless, several factors may influence the bond including surface preparation, adhesive thickness, test method, crosshead speed and material type (6). In this study, enamel was abraded with silicon carbide paper increasing its roughness. This method is used in laboratory research to standardize the specimen preparation, simulating clinical dentin/enamel preparation using a medium-grit diamond bur (16,21). Surface roughness creates an increased surface area and mechanical retention may have enhanced slightly on enamel (21). Moreover, removing the outer aprismatic enamel layer and reaching the inner prismatic enamel may also improve enamel bonding (21). The experimental design using the same tooth to test different materials is advised to minimize the effect of substrate on the composite resin factor (16). The use of only two sticks is a limitation of the tooth size and the number of the variations tested on each unit sample (15). However, it is advisable to have a smaller number of sticks for one composite but to have the same substrate tested for both study factors (composite resin – 2 sticks each; aging time – 2 sticks each).

The evolution of restorative materials tends to induce the clinicians to expect that new products result directly in a better performance. New technologies of the composite resin manufacturers aim to reduce shrinkage of the composite during polymerization. But the modifications of the composite resins do not always alter only one mechanical property, reflecting in a negative performance of the material because it is dependent of multifactorial aspects (2,5). Despite its low polymerization shrinkage, the silorane-based resin does not appear to be a better alternative then methacrylate resins. In this study was used a flat surface for enamel and dentin. Flat surface does not actually account for all the aspects involved in the residual shrinkage stress generated after resin polymerization. The C factor is much smaller on flat surfaces than in conventional dental cavities. However, using this method to measure the post-gel shrinkage, where the composite is inserted over the strain-gauge, revealed that the shrinkage stress of Filtek LS is significantly lower than that of Filtek Supreme (5,25). Therefore the lower bonding strength performance of silorane composite resulted from the inefficiency of the adhesive procedure and mechanical interaction with the composite resin. Moreover, bonding to enamel was significantly higher than to dentin for both composites and 3 months aging appears to be not long enough to promote changes in dentin and enamel μTBS, given the used restorative systems. Additional *in vitro* tests that evaluate wear and fracture resistance and mainly the randomized clinical trials with longer follow-up period should be performed to verify the clinical behavior of this material, since the oral environment has characteristics that cannot be faithfully reproduced in laboratory studies. In addition, due the short storage time and intrinsic limitations of laboratory studies, this research outcomes were limited by the immediate bonding of the restoration, different from what happens usually in the oral environment, as in this study the C factor had little influence because the restored surface was flat.

Resumo

O objetivo deste estudo foi avaliar a resistência adesiva por meio do teste de microtração (μTBS) entre dois substratos (esmalte e dentina) considerando dois fatores em estudo: Tipo de resina [metacrilato (Filtek Supreme) ou silorano (Filtek LS)] e tempo de envelhecimento (24 horas ou 3 meses). Vinte molares humanos foram selecionados e divididos em dois grupos (n=10) considerando dois substratos dentários, esmalte e dentina. O esmalte e a dentina de cada dente foram divididos em duas metades, por meio de uma lamínula. Cada dente foi restaurado usando ambas as resinas testadas, seguindo instruções do fabricante. As amostras foram seccionadas, resultando em quatro palitos para cada tipo de resina. Metade

dos palitos foi testada após 24h e o restante após três meses. O ensaio de microtração (μTBS) foi conduzido numa velocidade de 0,05 mm/s. Os dados foram analisados usando three-way ANOVA e teste de Tukey HSD (α= 0,05). Diferença significante foi encontrada para o fator resina e substratos ($p<0,05$), porém não houve influência do tempo de envelhecimento e interações entre fatores estudados. A resina à base de metacrilato apresentou maior resistência adesiva do que a silorano. A adesão em esmalte foi significativamente maior do que em dentina, independente da resina e do tempo de envelhecimento. Três meses de armazenamento não foram suficientes para causar degradação da interação adesiva, para ambas as resinas compostas, no esmalte e na dentina.

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