

Repair Strength in Simulated Restorations of Methacrylate- or Silorane-Based Composite Resins

Rafael Leonardo Xediek Consani¹, Tatiane Marinho¹, Atais Bacchi², Ricardo Armini Caldas¹, Victor Pinheiro Feitosa³, Carmem Silvia Pfeifer⁴

¹Department of Prosthodontics and Periodontology, Piracicaba Dental School, Universidade de Campinas, Piracicaba, SP, Brazil
²UPF – Universidade de Passo Fundo, Passo Fundo, RS, Brazil
³Post-Graduation Program in Dentistry, Health Sciences Center, UFCE - Universidade Federal do Ceará, Fortaleza, CE, Brazil
⁴Biomaterials and Biomechanics, OHSU, Portland, OR, USA

Correspondence: Rafael Leonardo Xediek Consani, Avenida Limeira 901, 13414-903 Piracicaba, SP, Brasil. Tel: +55-19-2106-5296. e-mail: rconsani@fop.unicamp.br

The study verified the bond strength in simulated dental restorations of silorane- or methacrylate-based composites repaired with methacrylate-based composite. Methacrylate- (P60) or silorane-based (P90) composites were used associated with adhesive (Adper Single Bond 2). Twenty-four hemi-hourglass-shaped samples were repaired with each composite (n=12). Samples were divided according to groups: G1= P60 + Adper Single Bond 2 + P60; G2= P60 + Adper Single Bond 2 + P60 + thermocycling; G3= P90 + Adper Single Bond 2 + P60; and G4= P90 + Adper Single Bond 2 + P60 + thermocycling. G1 and G3 were submitted to tensile test 24 h after repair procedure, and G2 and G4 after submitted to 5,000 thermocycles at 5 and 55 °C for 30 s in each bath. Tensile bond strength test was accomplished in an universal testing machine at crosshead speed of 0.5 mm/min. Data (MPa) were analyzed by two-way ANOVA and Tukey's test (5%). Sample failure pattern (adhesive, cohesive in resin or mixed) was evaluated by stereomicroscope at 30× and images were obtained in SEM. Bond strength values of methacrylate-based composite samples repaired with methacrylate-based composite (G1 and G2) were greater than for silorane-based samples (G3 and G4). Thermocycling decreased the bond strength values for both composites. All groups showed predominance of adhesive failures and no cohesive failure in composite resin was observed. In conclusion, higher bond strength values were observed in methacrylate-based resin samples and greater percentage of adhesive failures in silorane-based resin samples, both composites repaired with methacrylate-based resin.

Key Words: dental composite, methacrylate, silorane, repair, bond strength.

Introduction

Despite the development of new restorative materials and recent clinic techniques, the dental restorations made with composite resins have shown limited performance in long time, which can lead to a restorative repetitive cycle, with possible weakening of tooth due to mineralized tissue loss. In this context, the repair in composite restorations appears to be a less invasive alternative method when correctly indicated (1).

Chemical solutions may affect the physical and mechanical properties of these materials by the effects of the solvent uptake and elution of components. However, in long-term the elution of degradation products in the oral cavity (2) compromises the longevity of the dental restoration and decreases the capacity of restoration repair (3). In addition, different surface treatments produce different bond strengths for the repair of recent restorations of silorane- and methacrylate-based composites (4). These factors are the rationale to verify the behaviour of repair in the composite restorations.

Surface roughness, bond type, repair materials and aging are variables that affect the adhesive strength between aged and recently added resin. In repaired restorations, the bond between aged and repair resins and also between the

layers of new resin is difculted by the inhibiting layer of polymerization caused by oxygen. Nevertheless, the amount of unsaturated double bonds decreases with aging, reducing the bond strength between increments (aged and repair). Thus, some techniques are recommended to improve the bond strength of aged composite resins. Micro-interlocking (roughness) and other procedures are based on attempts to improve the resin adhesion by links between the new polymeric matrix and the filler particles of the aged resin (5), and it depends on whether the material is used as filling or for the repair of material (6). Surface roughness can be mechanically obtained by means of diamond points or blasting with aluminum oxide particles and chemically etched with hydrofluoric or phosphoric acid. Therefore, both procedures are employed to remove the aged layer of resin and create roughness for increasing the bond strength.

Silanes and unfilled resins are traditionally used as bond agents for restoration repairs. Silanes promote chemical bond between resin and filler particles, and may also increase the ability to wet the adhesive onto the surface roughness. Moreover, the adhesive promotes chemical bond between the organic matrices of the new composite and the old resin to be repaired (5). Different from the traditional system of polymerization, silorane-based composites use the cationic

polymerization mechanism with lower shrinkage values and polymerization stress at tooth-restoration interface. Consequently, it has been alleged that some drawbacks are avoided or minimized, such as cusp deflection, crack propagation in enamel and failures at the bond interface, resulting in microorganism contamination and consequent pulp damage (7).

Bond strength of aged methacrylate- or silorane-based composites using the same repair resin related to surface treatments was recently evaluated (8). However, siloranes have been claimed as materials to be withdrawn from the dental market. The aim of this study was to verify the bond strength of repairs in simulated restorations of methacrylate- or silorane-based composite resins using methacrylate-based composite resin. The tested hypothesis was that bond strength values of repairs made with methacrylate-based resin in methacrylate- or silorane-based simulated restorations would be similar.

Material and Methods

Hemi-hourglass Shaped Samples Preparation

Twenty-four hourglass-shaped matrices (13 mm long, 2 mm thick, 6 mm wide at the ends and 3 mm wide in the central region) of Filtek P60 (methacrylate-based; 3M ESPE, St. Paul, MN, USA) and Filtek P90 (silorane-based; 3M ESPE) resin composites were obtained using silicone molds (Zetalabor; Zhermack, Rovigo, Italy) (8) (Table 1). Four composite increments were used to fill the mold, each increment activated by a light-curing unit (Ultra-Lume LED; Ultradent, South Jordan, UT, USA) at 800 mW/cm² for 20 s. A glass plate was used to press the last increment during photoactivation. Next, the matrices were stored in an oven at 37 °C for 6 months in distilled water.

After storage, the hourglass-shaped matrices were sectioned in the central portion obtaining 48 hemi-hourglass matrices for each composite resin. The bond surfaces of the composite matrices were submitted to mechanical abrasion with 600-grit Al₂O₃ paper (Norton, Guarulhos, SP, Brazil) for 10 s, ultrasonically cleaned (Vitasonic; Vita, Germany) in distilled water for 10 min and air jet dried. The bond surface was etched with a thin layer of silane (Angelus, Londrina, PR, Brazil) with 1 min drying. A thin layer of adhesive

(Adper Single Bond 2; 3M ESPE) was applied on the bond surface for 10 s and air thinned according to manufacturer's instructions. The adhesive activation was made with a LED light-curing unit (Ultradent) at 800 mW/cm² for 20 s. After these procedures, the composite hemi-hourglass-shaped matrices were divided according to following groups (n=12): G1: P60 + Adper Single Bond 2 + P60; G2: P60 + Adper Single Bond 2 + P60 + thermocycling; G3: P90 + Adper Single Bond 2 + P60; and G4: P90 + Adper Single Bond 2 + P60 + thermocycling.

Repair Procedure of the Hemi-Hourglass-Shaped Samples

Each hemi-hourglass-shaped composite matrix was placed into the silicone mold and the remaining part was filled with four increments of restorative composite, according to the experimental groups established in the study. The first three increments were photoactivated for 20 s each one and the last increment pressed by a glass plate during photoactivation for 20 s. After mold removal, the repaired sample was additionally activated for 40 s. All activation procedures were carried out with a LED unit (Ultradent) at 800 mW/cm².

G1 and G3 repaired samples were tensioned after storage at relative humidity for 24 h, while the G2 and G4 repaired samples were tensioned after 5,000 thermal cycles (MSCT thermocycler; Geraldini ME, São Carlos, SP, Brazil) at 5 and 55 °C in 30 s baths for each temperature.

Bond Strength Test

Repaired samples were fixed with cyanoacrylate glue (Super Bonder Gel; Loctite, Diadema, SP, Brazil) associated with instant cure accelerator (Tak Pak Accelerator; Loctite) in a Bencor-MultiT modified device adapted to an universal testing machine (4411 model; Instron, Canton, MA, USA) and tensioned at a crosshead speed of 0.5 mm/min until failure.

The transverse dimensions of the failures were measured with a digital caliper (Mitutoyo; Tokyo, Japan) and the values utilized for bond area calculation. Data for bond strength were evaluated for normality by Kolmogorov-Smirnov and the heterocedasticity of variances by Levene's tests. Data distribution was normal and the variances were

Table 1. Restorative composites and formulation

Material	Resin	Organic matrix	Fillers
Filtek P90*	Silorane	3,4-epoxycyclohexylethylcyclo polymethylsiloxane, Bis 3,4-epoxycyclohexylethylphenylmethysilane	76 wt.% quartz, yttrium fluoride
Filtek P60 [†]	Dimethacrylate	Bis-GMA, UDMA, Bis-EMA	84 wt.% zirconia/silica

Lot number = *N136711; [†] N138420. Bis-GMA: Bisphenol A glycidyl dimethacrylate; UDMA: urethane dimethacrylate; Bis-EMA: ethoxylated Bisphenol A dimethacrylate.

homogenous. Following, the data (MPa) were submitted to two-way ANOVA and the mean values compared by the Tukey's test ($\alpha=0.05$). The analyzed factors were composite resin and treatments (24 h and thermocycled).

Failure Pattern

Failure pattern of the failed surface was evaluated with a stereomicroscope (EMZ-TR; Meiji Techno, Tokyo, Japan) at 30 \times magnification by a single examiner and the results analyzed by all authors. Failure patterns were considered as adhesive, cohesive in resin or mixed. Representative failure of each group was processed for SEM analysis as follows: both parts of the failed sample were paired, air dried, mounted on aluminum stub, gold coated and SEM (JSM-

5600LV, JEOL; Tokyo, Japan) examined at 15 kV.

Results

Table 2 shows that the methacrylate-based composite samples repaired with methacrylate-based composite presented higher and statistically significant bond strength values ($p=0.002$) compared to silorane-based samples. The thermocycling procedure decreased significantly the bond strength values for all repaired samples ($p=0.007$).

Table 3 shows prevalence of adhesive failures in all groups (%). G1 (24 h) and G2 (thermocycled) methacrylate groups showed 41% and 32% of mixed failures, respectively, whereas G3 (24 h) and G4 (cycled) silorane groups presented 18% and 0% of mixed failures, respectively. No cohesive failure in composite resin was observed in the groups with and without thermocycling. SEM evaluations of failures

Table 2. Means and standard deviation of the bond strength values (MPa) for methacrylate- or silorane-based samples

Based-sample	24 h	Thermocycled	Mean
Methacrylate (G1 and G2)	6.95 \pm 1.8 aA	6.04 \pm 1.8 bA	6.50 \pm 0.6 A
Silorane (G3 and G4)	5.80 \pm 1.7 aB	4.27 \pm 1.2 bB	5.03 \pm 1.1 B
Mean	6.37 \pm 0.8 a	5.16 \pm 1.2 b	-

Different small letters in rows and capital letters column differ by Tukey's test ($\alpha<0.05$).

Table 3. Sample failure pattern (%) for methacrylate- or silorane-based samples

Failure	Methacrylate		Silorane	
	G1 (24 h)	G2 (cycled)	G3 (24 h)	G4 (cycled)
Adhesive	59%	68%	82%	100%
Mixed	41%	32%	18%	0%

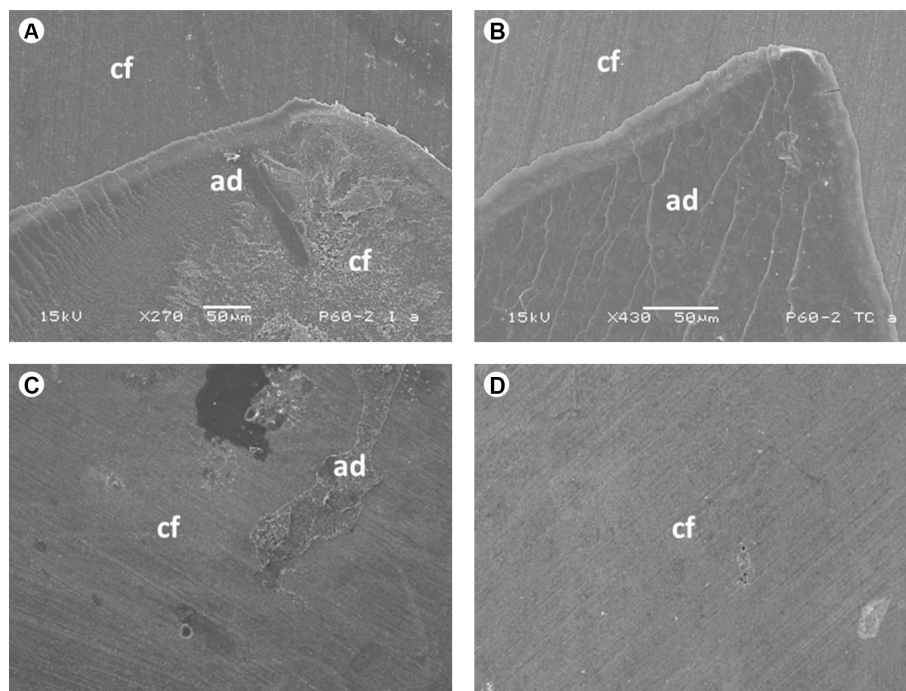


Figure 1. Representative SEM images of debonded samples. A: G1 (P60 + P60 24 h): Mixed failure involving old composite (cf) and adhesive layer (ad). B: G2 (P60 + P60 cycled): Mixed failure in old composite (cf) and adhesive substrate (ad). Although G1 and G2 groups presented statistically significant difference for bond strength values, the SEM images shows similar mixed failures involving old material and adhesive layer. C: G3 (P90 + P60 24 h): Large area of adhesive failure between the old composite (cf), the adhesive layer (ad) and a small region of adhesive. D: G4 (P90 + P60 cycled): Complete adhesive failure showing only old composite (cf).

observed in G1 (24 h), G2 (cycled), G3 (24 h) and G4 (cycled) groups are shown in Figure 1.

Discussion

This study evaluated the bond strength of methacrylate- or silorane-based samples repaired with methacrylate-based composite before and after thermocycling procedures. The tested hypothesis that bond strength values of repairs with methacrylate-based resin in methacrylate- or silorane-based simulated restorations would be similar was not accepted.

Repairs of composite resins are usually performed months or years after the dental restoration because exposition time in the oral environment promotes water sorption, chemical degradation and leaching of components. In addition, free radicals are responsible for the adhesion among different layers of the restorative composite resin (9). It is possible that the chemical adhesion between new and old resins did not establish a reliable bonding in chemical conditions, considering that the quantity of free radicals decreases with the aging of dental restoration (10).

These conditions related to adhesion can affect the repair success, changing the bond strength value due to the microstructural characteristics and composition of the composite resin (3). Since silorane is considered a tetra-functional molecule with greater molecular weight than other components used in most methacrylate-based materials, the component leached levels are less evident, even considering that the degree of conversion of the material is smaller (11). However, epoxy groups polymerized by cationic mechanism may be less available for chemical reaction on the material surface than the polymeric products. This fact would explain the difference in bond strength when compared with composite resins, where the methacrylate-based composite resin showed greater bond strength than silorane-based composite (Table 2).

Mechanical interlocking is the most significant factor to increase the bond strength of resin repairs (12) and incremental shear bond strength was achieved by aluminum oxide sandblasting and silica coating (13). Thus, mechanical surface treatments have been suggested to increase the roughness and free surface energy. This procedure also removes the superficial layer of resin deteriorated by the oral environment (4), and increases the possibility of the material to offer a greater amount of carbon with the available free linkage (14). Moreover, surface treatment with diamond points and hydrofluoric acid etching promotes smaller bond strength when compared to other abrasive treatments (13).

A previous study considered the silane etching as a decisive factor for adhesion of methacrylate-based resin on siloxane surfaces (15). Silanes and free-filler resins are traditionally used as bond agents for repair due to the

capacity for linkage with filler particles and to bond with the organic matrix (3).

Thermocycling is more effective for degradation of composite resins than other aging methods (16). The number of cycles is considered the most influential factor to alter the effect of thermocycling. According to ISO, 500 cycles in water between 5 and 55 °C are considered appropriate for aging dental materials (17). If an analogy is possible, results from previous work showed that 500 cycles were not enough to affect the bond strength between composite resins and dentin (18), whereas the thermocycling effect on the bond strength of composite resins was more effective when performed at 5,000 cycles (16). In the current study, it may be noted that the bond strength decreased when the samples were submitted to thermocycling and the values presented statistically significant difference among groups (Table 2). This result may be explained by the degradation of the adhesive interface due to water sorption, chemical changes and consequent leaching of some components.

Table 3 shows the failure pattern (%) of the debonded samples. Although showing prevalence of adhesive failures, G1 (24 h) and G2 (cycled) methacrylate groups presented also mixed failures. In the G1, the percentage of mixed failures was greater compared to G2. Probably, less deterioration of the adhesive interface of the G1 samples was responsible for this result compared to thermocycled G2 group. The G3 (24 h) and G4 (cycled) silorane groups showed prevalence of adhesive failures, result due to the lesser amount of free carbons to react with the repair resin, considering that this material is a silorane-based composite resin. When silorane groups were compared, G3 samples presented small percentage of mixed failures, while G4 showed only adhesive failures, results consistent with the difference of bond strength values observed in these groups. Previous works showed cohesive failures more frequently than adhesive failures when the silane agent was applied or when silorane composite was used for repair (13); groups with silane and bonding agent had the highest strength values, showing a reasonable number of cohesive failures (19). In the present study, although repaired with methacrylate-based material, the group with silorane-based material showed predominance of adhesive failures. A previous study showed that after aluminum oxide sandblasting, the aged silorane resin repaired with either silorane resin composite with Filtek LS system adhesive or methacrylate resin composite with methacrylate dental adhesive presented primarily adhesive failures in all groups (20).

Conversely, due to different effect of the microstructure on the mechanical behavior of the composite resin (3), there is no standard protocol for repair procedures in all clinical situations, as the knowledge of the material composition is a crucial factor for the success of repair (21). However,

although thermocycling has decreased the bond strength of methacrylate-based samples, this procedure could be considered a reliable clinical alternative for situations in which the repair can be made with the same material of the restoration, considering the percentage of mixed failures observed for the G1 and G2 groups (Table 3). In terms of clinical performance, it was shown that after two years the result for silorane-based composite was similar to the dimethacrylate-based composite, except for marginal discoloration in the silorane-based restorations (22).

Although a statistically significant difference was observed for bond strength values between G3 and G4 groups, both silorane samples showed predominance of adhesive failures. G3 shows small amount of adhesive layer on a larger region of old substrate, whereas G4 presented totally adhesive failure. In conclusion, higher bond strength values were observed in methacrylate-based resin samples and greater percentage of adhesive failures in silorane-based resin samples, both composites repaired with methacrylate-based resin.

Resumo

O objetivo neste estudo foi verificar a resistência de união em restaurações simuladas de compósitos baseados em metacrilato ou silorano reparadas com compósito à base de metacrilato. Compósitos baseados em metacrilato (Filtek P60; 3M ESPE) ou silorano (Filtek P90; 3M ESPE) foram associados com adesivo (Adper Single Bond 2; 3M ESPE). Vinte e quatro amostras em forma de semi-ampulhetas foram reparadas com cada material (n=12), conforme os grupos experimentais: G1- P60 + Adper Single Bond 2 + P60; G2- P60 + Adper Single Bond 2 + P60 + termociclagem; G3- P90 + Adper Single Bond 2 + P60; e G4- P90 + Adper Single Bond 2 + P60 + termociclagem. Os grupos G1 e G3 foram submetidos ao ensaio de tração após 24 horas do procedimento de reparo e os grupos G2 e G4 depois de submetidos a 5.000 ciclos térmicos de 5 e 55 °C por 30 s em cada banho. O teste de resistência à tração foi efetuado em máquina universal atuando numa velocidade de 0,5 mm/min. Os dados (MPa) foram submetidos a ANOVA a dois fatores e teste de Tukey (5%). O padrão de fratura das amostras (adesivo, coesivo em resina ou misto) foi avaliado em estereomicroscópio com aumento de 30x e imagens representativas foram obtidas em MEV. Os valores de resistência à tração das amostras feitas com compósito à base de metacrilato e reparadas com compósito à base de metacrilato (G1 e G2) foram maiores do que nas amostras feitas com compósito à base de silorano e reparadas nas mesmas condições (G3 e G4). A termociclagem diminuiu os valores de resistência à tração para ambos os compósitos. Todos os grupos mostraram predominância de fraturas adesivas e nenhuma falha coesiva foi observada em compósito. Em conclusão, valores maiores de resistência à tração foram observados em amostras de resina à base de metacrilato e maior percentagem de fraturas adesivas nas amostras de resina à base de silorano, ambos os compósitos reparados com resina à base de metacrilato.

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