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Knoop Hardness and Effectiveness of Dual-Cured Luting Systems and Flowable Resin to Bond Leucite-Reinforced Ceramic to Enamel

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Abstract

Purpose: The aim of this study was to evaluate the Knoop microhardness and microshear bond strength (MSBS) of dual-cured luting systems and flowable resin bonded to leucite-reinforced ceramics and enamel.
Materials and Methods: Eighty bovine incisors were randomly divided into four groups per test (microhardness and microshear; n = 10) according to the bonding procedure: Excite DSC/Variolink, Clearfil SE Bond/Panavia F, Adper Scotchbond Multi-Purpose Plus/RelyX ARC, and Adper Single Bond 2/Filtek Z350 Flow. For the KHN measurement, the cement was applied on the enamel surface and light-cured through a ceramic disk (5 mm diameter × 1.2 mm thick). Five indentations were performed in each specimen and measured at HMV-2. For the microshear test, two cylinders of a leucite-reinforced ceramic (1 mm diameter × 2 mm height) were bonded to the enamel substrate in accordance with the bonding procedures previously established. One cylinder was tested 24 hours after cementation, and the other was subjected to thermocycling (2000 cycles) and then submitted to an MSBS test. The data from the hardness and bond strength tests were subjected to one- and two-way repeated-measures analysis of variance (ANOVA), respectively, and to Tukey's test ($\alpha = 0.05$).
Results: Scotchbond/RelyX ARC presented higher values of bond strength, while Single Bond/Z350 Flow showed lower values. The thermocycling promoted a reduction in the bond strength values for all groups. Panavia F presented higher values of KHN, and the flowable resin presented the lowest. RelyX ARC and Variolink presented intermediate values on hardness evaluation.
Conclusions: For ceramic cementation, dual-cured resin luting systems promoted more reliable bonding and microhardness values than the flowable resin.

During cementation of ceramic restorations, resin luting cements are light-activated through the indirect material, yielding light absorption and scattering before reaching the luting system.[1] Dual-cured resin cements were developed to guarantee the material's conversion even with low light intensity, ensuring adequate mechanical properties.[2] However, the original color of dual-cured resin cements may change over time, due to oxidation of the tertiary amine present in the systems, and this characteristic can jeopardize the esthetic appearance of the restoration, especially in thin ceramic veneers.[3]

Flowable resin composites are light-cured materials that interfere minimally with the esthetic stability of the ceramic restoration and can be used for the cementation of thin ceramic veneers. The mechanical properties of resin materials depend on the polymer structure[4] and degree of monomer conversion,[5] which are strictly related to the effective polymerization.[6] These parameters are important, as luting agents can promote an increase in the fracture strength of dental ceramics and, consequently, improve the clinical performance of the indirect restoration.[7,8] Knoop hardness assessment helps to predict the clinical performance of resin restorative materials and is related to its stiffness.[7,8]

Since no material satisfies all the required characteristics for an ideal luting system, the selection of the appropriate resin cement is conditional on its performance in some situations, such as bonding to the tooth and indirect restoration, and properties such as sorption and solubility, degree of conversion, fracture strength, Knoop hardness, and biocompatibility.[7,8] Therefore, the aim of this study was to evaluate the Knoop hardness and microshear bond strength (MSBS) to dental enamel of resin luting systems light-cured through leucite-reinforced ceramics. The hypothesis tested was that a flowable composite could be an effective alternative for veneer ceramic cementation, with similar bond and hardness performances compared to dual-cured resin cements.

Materials and methods

Specimen preparation

Eighty bovine incisors were selected, cleaned, and stored in a 0.5% chloramine T solution at 4°C for no more than a week. The roots were sectioned 1 mm above the cementoenamel junction using a double-faced diamond disk (K.G. Sorensen, São Paulo, Brazil). The buccal surface was ground flat using silicon carbide abrasive papers of increasing grit, no. 320 and no. 600 (Carborundum, Saint-Gobain Abrasives Ltda., Guarulhos, Brazil), under water cooling to obtain a flat enamel surface (8 mm^2). These teeth were observed using a stereomicroscope (Leica Microsystems, Heerbrugg, Switzerland) at 25× magnification to guarantee the enamel integrity.

The specimens were randomly divided into four experimental groups ($n = 10$) according to the resin luting system: G1 – Excite/Variolink II (EX/VAR), G2 – Clearfil SE Bond/Panavia F (CSE/PAN), G3 – Scotchbond Multi-Purpose Plus/RelyX ARC (SBMP/RX), and G4 – Adper Single Bond 2/Filtek Z350 Flow (SB/Z350F). The names, brand, batch, and composition of the resin materials used in this study are presented in Table 1. The bonding procedures for luting systems were as follows:

Group 1 (EX/VAR)

The enamel was acid-etched with 35% phosphoric acid (Scotchbond, 3M ESPE, St. Paul, MN) for 15 seconds and washed with distilled water for 15 seconds. The adhesive (EX) was applied on the enamel according to the manufacturer's instructions. The solvent was evaporated using a mild air stream and further light-curing for 10 seconds. For the Variolink II cement, base and catalyst pastes were mixed for 15 seconds, the ceramic was positioned with a 500-g standard weight and trans-ceramic light-curing was performed for 40 seconds.

Group 2 (CSE/PAN)

The adhesive primer (CSE) was applied on the enamel surface for 30 seconds, followed by bond application and light curing for 10 seconds. For the ceramic treatment, CSE primer was mixed with the porcelain bond activator and applied on the ceramic surface for 1 minute. Next, Panavia F cement base and catalyst pastes were mixed for 20 seconds, the ceramic was positioned with a 500-g standard weight, and trans-ceramic light curing was performed for 40 seconds.

Group 3 (SBMP/RX)

The enamel was etched with 35% phosphoric acid for 15 seconds and washed with tilled water for 15 seconds. The SBMP activator was applied on enamel followed by a 5-second mild air stream. The SBMP primer was applied followed by the 5-second air stream, with further application of the SBMP catalyst at the enamel and in the internal ceramic surface. For RelyX ARC, the base and catalyst pastes were mixed for 10 seconds, the ceramic was positioned with a 500-g standard weight, and trans-ceramic light curing was performed for 40 seconds.

Group 4 (SB/Z350F)

The enamel was acid-etched with 35% phosphoric acid for 15 seconds and washed with distilled water for 15 seconds. Next, two consecutive adhesive (SB) layers were applied for 10 seconds, a mild air stream was used to evaporate the excess solvent, and the specimens were light cured for 10 seconds. For Filtek Z350 Flow, the resin was applied, the ceramic was positioned with a 500-g standard weight, and trans-ceramic light curing was performed for 40 seconds.

Microshear bond strength test (MSBS)

The internal surface of IPS Empress Esthetic leucite-reinforced ceramic cylinders (1-mm diameter, 2-mm thick) was etched for 60 seconds with 10% hydrofluoridric acid (Dentsply, Providencia, Santiago, Chile), followed by the application of a silane agent for 60 seconds (Monobond S, Ivoclar Vivadent, Schaan, Liechtenstein). The adhesive and resin cement were light-cured using a halogen light (VIP – Bisco, Schaumburg, IL, 600 mW/cm^2). After this, the adhesive protocol was performed according to the respective group. For all specimens, the adhesive area was delimited using adhesive tape to avoid the overflow of luting agents beyond the ceramic luting area.

Two ceramic cylinders were cemented on each tooth crown, and 24 hours after the bonding procedure, one of the cylinders was subjected to an MSBS test using a thin metal wire (0.2-mm thick) in a universal testing machine (EZ-Test, Shimadzu Corp., Japan) at a 0.5 mm/min crosshead speed. Values were expressed in MPa.

After the immediate bond strength test, the remaining cylinder of each tooth was subjected to 2000 thermal cycles (MSCT – 3e ELQUIP, São Carlos, Brazil) with alternating baths of 30 seconds (5 ± 1°C, 37 ± 1°C, and 55 ± 1°C). After artificial aging, MSBS was carried out in a way similar to that described previously. After these procedures, data were subjected to two-way repeated-measures analysis of variance (ANOVA) and Tukey's test ($\alpha = 0.05$).

Table 1 Materials, batch numbers and composition of the products used in the study

Luting system	Manufacturer	Lot no.	Chemical composition
Adhesive: Excite	Ivoclar Vivadent	1177	Phosphonic acid acrylate, HEMA, Bis-GMA, methacrylates, silicon dioxide, ethanol, catalysts and stabilizers.
Resin cement: Variolink	Ivoclar Vivadent	01441	**Base:** Bis-GMA, UDMA and TEGDMA, barium glass, ytterbium trifluoride, glass fluorsilicate barium and aluminum oxides mixed spheroid. **Catalyst:** Bis-GMA, UDMA and TEGDMA, ytterbium trifluoride, glass and aluminum fluorsilicate barium and spheroid mixed oxide, benzoyl peroxide, stabilizer.
Adhesive: Clearfil SE Bond	Kuraray	00954A	**Primer:** Phosphate biacid metacriloiloxidecilo 10 (MDP), hydroxiethylmetacrilate 2 (HEMA), hydrophilic dimethacrylate, dl Alcanforoquinona, N, N-diethanol p-toluidine, water. **Bond:** Phosphate BIAC metacriloilixidecilo 10 (MDP), bisphenol A diglycidyl methacrylate (Bis-GMA), hydroxiethylmetacrilate 2 (HEMA), hydrophilic dimethacrylate, Alcanforquinonadl, N, N-diethanol p-toluidine, colloidal silicon dioxide silanized.
ED Primer	Kuraray	00147A	**Paste A:** 10-MDP, silanized silica, hydrophobic aromatic and aliphatic dimethacrylate, dimethacrylate hydrophobic photoinitiator, benzoyl peroxide. **Paste B:** silanized barium glass, sodium fluoride, sodium sulfinate aromatic dimethacrylate monomer, BPO.
Resin cement: Panavia F	Kuraray	00027B	**Primer A:** HEMA, 10-MDP, 5-NMSA, water, accelerator. **Primer B:** 5-NMSA, accelerator, water, sodium sulfinate aromatic
Adhesive: Scotchbond Multi-use Plus	3M ESPE	N130621	**Activator:** ethanol, sodium benzene sulfinic. **Primer:** Water, 2 - hydroxyethyl methacrylate, copolymer of acrylic and Itaconic acid (5AT). **Catalyst:** Bis-GMA, 2 - Hydroxyethyl methacrylate, benzoyl peroxide (3AP).
Resin cement: RelyX ARC	3M ESPE	N199496	**Paste A:** ceramics treated with silane, TEGDMA, Bis-GMA, silane-treated silica, dimethacrylate functional polymer. **Paste B:** ceramics treated with silane, TEGDMA, Bis-GMA, silane-treated silica, dimethacrylate functional polymer (EYFH).
Adhesive system: Single Bond	3M ESPE	BUBR	Water, alcohol, HEMA, Bis-GMA, dimethacrylate, photoinitiator system and copolymers of polyacrylic acid and poly-Itaconic.
Resin: Filtek Flow	3M ESPE	N124855	**Matrix:** BisGMA, TEGDMA, dimethacrylate polymer **Filler:** 47% zirconia / silica

Knoop hardness assessment

For the Knoop hardness evaluation (n = 10), an IPS Empress Esthetic ceramic disk was prepared (5-mm diameter, 0.6-mm thick for the ceramic coping, IPS Empress Esthetic, and 0.6 mm-thick feldspathic ceramic, A2 shade, totaling a ceramic specimen with a 1.2 mm thickness). The bond procedure on enamel was performed according to the protocols previously described. After the cement application, a Mylar strip was applied on the cement, and the ceramic disk placed over the polyester strip. The cement was light-cured for 40 seconds through the ceramic with the halogen light (VIP – Bisco, 600 mW/cm^2).

After curing, the ceramic disc was removed, and the specimens were stored at 37°C in the dark for 24 hours. For the Knoop hardness measurement, 16 indentations were performed on the top surface of the cement with a 25-g load and a 10-second dwell time using a microhardness tester (HMV-2T, Shimadzu Corp.).

Next, the mean of the 16 indentations was recorded, and the Knoop hardness number for each tooth was calculated. The results were subjected to one-way ANOVA and Tukey's test ($\alpha = 0.05$).

Results

Microshear bond strength

MSBS data were analyzed by two-way ANOVA. The factors "cement" (0.0001) and "artificial aging" (0.0065) were statistically significant; however, the interaction between the factors ("resin luting system" × "artificial aging") was not significant (0.9271). The results of the Tukey test are presented in Table 2.

SBMP/RX presented significantly higher bond strength than the other luting systems. CSE/PAN and EX/VAR were statistically similar and presented intermediate bond strength values, while the SB/Z350F showed lower enamel bond strength means compared to the other experimental groups. Regarding artificial aging, thermocycling decreased the bond strength values for all protocols tested.

Knoop hardness

The Knoop hardness data were evaluated by one-way ANOVA and Tukey's test ($\alpha = 0.05$) (Table 3). Panavia F obtained better microhardness values than Z350 flowable resin. Variolink II and RelyX ARC presented intermediate values, similar to Panavia F and Z350 flowable resin composite.

Table 2 Means (MPa; standard deviations) of the microshear bond strength for the groups tested, before and after artificial aging

Luting systems	Means (SD) 24 hours	Artifical aging (SD)	TUKEY
SBMP/RX	29.6 (9.4)	26.8 (4.9)	a
CSE/PAN	17.2 (5.1)	14.10 (4.7)	b
EX/VAR	16.8 (3.4)	14.1 (4.0)	b
SB/Z350F	10.7 (4.3)	7.3 (3.7)	c
	A	*B*	

Different letters represent significant statistical difference within the composite resin groups (two-way ANOVA and Tukey test ($p < 0.05$). The capital letters compare the effects of aging (artificial aging was significant for every group tested); lowercase letters compare the resin cements.

Table 3 Knoop hardness means (Standard Deviations) for the tested groups

Resin cement	N	Means (SD)	Tukey (5%)
PAN	10	49.7 (12.6)	A
VAR	10	43.8 (16.2)	AB
RX	10	39.6 (8.9)	AB
Z350F	10	35.0 (9.7)	B

Different letters represent significant statistical difference within the composite resin groups (one-way ANOVA and Tukey test ($p < 0.05$).

Discussion

Dual-cured resin cements are suitable materials for luting indirect restorations.[9] However, these agents can present color alteration due to the oxidation of the tertiary amine, which can compromise the esthetics of the ceramic restorations.[10] The aim of this study was to determine whether a flowable resin, a color-stable resin material, is a reliable alternative for cementing ceramic restorations. The results of this study showed that the hypothesis tested, that flowable composite resin would present similar microhardness and bonding effectiveness to those of dual-cure resin cements, was rejected.

Flowable resin showed the lowest Knoop hardness values, statistically different from Panavia F. This result can be partially explained by the mode of curing for the flowable resin. Filtek Flow is a light-cured material, and the reduced irradiance that reaches the resin after passing through the ceramic probably is not capable of promoting an adequate degree of conversion of the resin, reducing the hardness of the cured material.[11]

The filler amount of the materials can be another factor involved in the results. The resin cements Panavia F, RelyX ARC, and Variolink II present 78%wt, 73.4%wt, and 67%wt of filler, respectively, while Filtek Flow contains only 47%wt. According to Kumbuloglu et al,[12] the increased filler content in the resin cement promotes high hardness values for the material, explaining the results of the present study. The other resin cements tested (RelyX ARC, Variolink II) present slightly lower filler amounts than Panavia F. This was the probable cause for the results obtained for the Knoop hardness measurement, presenting intermediary values, similar to that of Panavia F and the flowable resin.

For the MSBS test, the resin luting system SBMP/RX showed the best values compared to the other materials tested. The adhesive protocol of the Scotchbond Multi-Purpose Plus (activator, primer, and catalyst) can promote adequate sealing due to the interlocking caused by the acid etching and the microporosities promoted by this procedure.[13] Another factor that can contribute to the higher bond strength values is the higher amount of benzoyl peroxide present in the catalyst, which can improve the quality of the cement conversion in the interface and the chemical adhesive-cement interaction.[14] The resin luting systems CSE/PAN and EX/VAR presented lower bond strength values than the SBMP/RX, but higher values than SB/Z350F. PAN was used with the self-etching adhesive CSE. This type of adhesive promotes high bond strength to dentin, but when used on the enamel, the results are not so reliable.[15] The poor bonding performance between the adhesive system and the enamel could have jeopardized the bond strength of CSE/PAN.

EX is an etch-and-rinse adhesive that requires previous acid etching to be applied on the dental substrate before bonding. Despite this, the results were intermediary, similar to CSE/PAN. This could have occurred due to the composition of the adhesive. EX presents a high amount of Bis-GMA and UDMA, monomers with high viscosity,[16] which can make the optimal interlocking in the enamel porosities difficult, reducing the quality of the bonding.

SB/Z350F presented the worst results for bond strength. The Z350 flow presents high polymerization shrinkage, which may induce shrinkage stress in the bonding interface, resulting in lower MSBS values,[17] such as those obtained in the present study.

Thermocycling was used to mimic the natural aging process of restorations in vitro, evaluating the behavior of restorative materials exposed to conditions similar to those found in the oral environment.[18] The aged specimens presented lower bond strength values than the groups tested 24 hours after bonding. This result can be attributed to stress concentration in the resin-filler interface during the thermal cycles due to the temperature variation, causing loss of filler particles and exposure of the resin matrix.[19] Thermocycling with extreme temperature changes can cause dimensional changes of the material, forming fracture lines in the bonding interface and resin cement as well. This may lead to fractures in the material, decreasing the bond strength of the composite restorative.[19]

The present study demonstrated that the flowable resin, a color-stable material, can be used to fix ceramic restorations to enamel; however, this material promoted lower bond strength values than the dual-cure resin cements tested, a fact that should be considered in the cementation procedure, as reduced bond strength can compromise the durability of the indirect restoration over the long term. Thus, for ceramic cementation, dual-cured resin luting systems promoted more reliable bonding and microhardness values than the flowable resin, which should be used for luting procedures with caution. Thereby, future studies evaluating the bond strength and physical properties of flowable resins for the cementation of thin ceramic veneers must be performed, since they are expected to present better physical and mechanical properties when properly cured.

Conclusions

The light-cured flowable resin composite used in combination with the Adper Single Bond 2 bonding system showed inferior Knoop hardness and lower bond performance compared to the dual-cured resin cements tested.

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