ORIGINAL RESEARCH
Dental Materials

Effect of light attenuation through veneers on bond strength of adhesives with photoinitiator combinations

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Abstract: This study aimed to evaluate the effect of light attenuation through ceramic veneers and resin cement on degree of conversion (DC), cohesive strength (CS), and microshear bond strength (μSBS) of experimental adhesive systems. Experimental etch-and-rinse and self-etch adhesives were combined with different ratios of camphorquinone (CQ) and diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) photoinitiators: CQ-only; 3CQ:1TPO; 1CQ:1TPO; 1CQ:3TPO and TPO-only. Square-shaped ceramic veneer (IPS Empress Esthetic, Ivoclar Vivadent) (n = 10; 10mm long x 10mm wide x 0.5mm thick) and resin cement specimens (Variolink Esthetic LC, Ivoclar Vivadent) (n = 10; 10 mm long x 10 mm wide and 0.3 mm thick) were prepared. Light transmittance of a multiple-peak LED (Bluephase G2, Ivoclar Vivadent) was measured through restorative materials using a spectrometer (n = 5). Adhesive specimens were analyzed for DC, CS, and μSBS by light-curing the adhesive with or without (control) ceramic veneer, and with resin cement fixed to output region of the light-curing tip (n = 10). Data were submitted to ANOVA and Tukey's test ($\alpha = 0.05$). Total light transmittance through the restorative materials was attenuated, and this attenuation was more evident for the violet spectrum. The DC for the TPO groups in ratios up to 1CQ:1TPO was similar to the control. 1CQ:3TPO showed lower values for CS. μSBS was reduced for all groups with light attenuation, but lower values were observed for 1CQ:3TPO and TPO-only. In conclusion, light transmission was reduced with interposed restorative materials. Adhesives combined with CQ and TPO up to 1CQ:1TPO showed greater cure efficiency and mechanical properties compared with a higher amount of TPO.

Keywords: Photoinitiators, Dental; Ceramics; Adhesives.

Introduction

Contemporary simplified adhesive systems (two-step etch-and-rinse and one-step self-etch) have hydrophilic primers combined with hydrophobic dimethacrylates. Today's adhesive systems also contain solvents to increase hydrophilicity, penetrability, and polymerization, which usually occurs in the presence of moisture.[1,2] Camphorquinone (CQ) and tertiary amine co-initiators (such as ethyl 4-dimethylaminobenzoate, EDMAB) are the most common photoinitiating systems used in dental

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adhesives and composites.[3] However, CQ is relatively hydrophobic and has difficulty initializing the polymerization of water-soluble monomers, such as HEMA, in aqueous solutions.[4] This property is conducive to nanophase separation, where the adhesive layer behaves like a permeable membrane after polymerization. In so acting, it allows water to flow from the underlying dentin substrate to the top of the adhesive layer.[5] Additionally, the low pH of adhesives may neutralize the tertiary amine from an acid-base reaction, especially with regard to one-step self-etch adhesives.[6]

For this reason, diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) has been studied as an alternative photoinitiator to CQ/amine in adhesive systems.[4,7,8,9] TPO is a Type I photoinitiator, and does not require an amine-based co-initiator to form free radicals, as occurs with CQ. This "amine-free" photoinitiator produces free radicals by a direct cleavage process.[10]

TPO has been shown be a more desirable photoinitiator in hydrophilic adhesives, because of its higher curing efficiency in water-containing experimental adhesives.[3] Studies have demonstrated the advantage of TPO over CQ regarding cure efficiency, hydrophilicity, and color stability.[3,9,11,12] However, the behavior of adhesive systems containing TPO photoactivated under ceramic restorations fixed with resin cement should always be evaluated. Ceramic veneers often require photoactivation of the adhesive simultaneously with the resin cement, because a previously polymerized adhesive film may interfere with the adaptation of this type of ceramic restoration. In this situation, the amount of energy that reaches the adhesive layer is an important aspect to consider.

It has been proven that light attenuation occurs through ceramic veneers.[11,13,14] This attenuation is affected by ceramic thickness, shade, intrinsic porosity, and crystalline structure. The characteristics of resin cements, such as composition, filler size, and differences in refractive index among the components, can interfere with light transmittance.[15,16] Another factor to consider is the light absorption by the photoinitiator. It has been proven that the smaller the wavelength, the higher the light attenuation through the same material.[12,17] This finding could apply to and hence impair TPO activation, since the absorption range of TPO in the violet wavelength is 380-420 nm, which is shorter than that of CQ (420-495nm).[10] Blue light is attenuated through ceramic veneers, even though the light intensity delivered to the underlying material is typically sufficient for light curing.[14,18]

Therefore, the aim of this study was to evaluate the influence of blue and violet light transmittance through ceramic veneer and resin cement on the degree of conversion, cohesive strength, and microshear bond strength of experimental etch-and-rinse and self-etch adhesive systems containing two different photoinitiators, either each alone or both combined in different ratios. The research hypotheses tested were: 1- the interposition of the ceramic veneer and the resin cement layers will influence light transmittance to the adhesive layer; 2- the interposition of the ceramic veneer and the resin cement layers will affect cure efficiency, cohesive strength, and bond strength of the adhesive system layer; 3- the use of different photoinitiator systems will affect cure efficiency, cohesive strength, and bond strength.

Methodology

Manipulation of adhesive systems

Experimental three-step etch-and-rinse and two-step self-etch adhesive systems were formulated. Table 1 lists the monomers and solvents used in the experimental primers and adhesives of the etch-and-rinse and self-etch adhesive systems, respectively. The primer monomers of each type of adhesive system (etch-and-rinse and self-etch) were blended using a centrifugal mixing device (SpeedMixer, DAC 150.1 FVZ- K, Hauschild Engineering, Hamm, North Rhine-Westphalia, Germany). The solvents were then added to each blend, according to the percentages described in Table 1. The experimental adhesive monomers of both adhesive systems were also blended using a centrifugal mixing device. Then, the different molar concentrations of CQ-amine (1:1) and TPO were added as described in Table 2. The photoinitiator combination ratios were: CQ-only (100%); 3CQ:1TPO (75%:25%); 1CQ:1TPO (50%:50%);

Table 1. Monomers and solvents used to formulate the experimental etch-and-rinse (ER) and self-etch (SE) adhesive systems.

Material	Chemical	Concentration (wt%)	Manufacturer (address)
Primer (ER)			
Monomers*	GDMA	15	Esstech Inc. (Essington, USA)
	HEMA	10	Sigma Aldrich (St. Louis, USA)
	UDMA	10	Sigma Aldrich
	TEGDMA	10	Sigma Aldrich
Solvent	Ethanol	55	Dinamica Ltda. (Indaiatuba, Brazil)
Bond (ER)			
Monomers*	UDMA	35	Sigma Aldrich
	BisEMA	45	Esstech Inc.
	TEGDMA	10	Sigma Aldrich
	GDMA	10	Esstech Inc.
Primer (SE)			
Monomers*	GDMA-P	15	Synthetized as previously described[23]
	HEMA	10	Sigma Aldrich
	UDMA	10	Sigma Aldrich
	TEGDMA	10	Sigma Aldrich
Solvents	Deionized water	15	Dinamica Ltda.
	Ethanol	40	Dinamica Ltda.
Bond (SE)			
Monomers*	UDMA	35	Sigma Aldrich
	BisEMA	45	Esstech Inc.
	TEGDMA	10	Sigma Aldrich
	GDMA-P	10	Synthetized as previously described[23]

*Glycerol dimethacrylate (GDMA); Hydroxyethyl methacrylate (HEMA); Urethane dimethacrylate (UDMA); Triethylene glycol dimethacrylate (TEGDMA); Ethoxylated bisphenol-A dimethacrylate (BisEMA); 1,3 glycerol dimethacrylate phosphate (GDMA-P).

Table 2. Photoinitiator systems used in the etch-and-rinse and self-etch adhesives.

Photoinitiator Systems*	Molar ratio	Concentration (wt%)		
	CQ:TPO	CQ	EDMAB	TPO
CQ-only	01:00	0.15	0.15	0
3CQ:1TPO	03:01	0.1125	0.1125	0.0625
1CQ:1TPO	01:01	0.075	0.075	0.125
1CQ:3TPO	01:03	0.0375	0.0375	0.1875
TPO-only	00:01	0	0	0.25

*Camphorquinone (CQ); Ethyl 4-(dimethylamino)benzoate (EDMAB); Diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO).

1CQ:3TPO (25%:75%) and TPO-only (100%). CQ and TPO concentrations were calculated in an equimolar ratio. Later, the EDMAB concentration was calculated in a 1:2 CQ:EDMAB ratio.

Ceramic specimen preparation

Square-shaped ceramic specimens simulating ceramic veneer restorations with dimensions of 10 mm long x 10 mm wide x 0.5 mm thick were fabricated using IPS Empress Esthetic (Ivoclar Vivadent, Schaan, Liechtenstein) shade ET2, following the manufacturer's instructions (n = 10).

Resin cement layer specimen preparation

Square-shaped specimens of resin cement layers (Variolink Esthetic LC, shade light+, Ivoclar Vivadent, Schaan, Liechtenstein) with dimensions of 10 mm long x 10 mm wide x 0.3 mm thick were made using rubber molds. Each resin cement specimen was photoactivated for 20 s (n = 10).

Light transmittance analyses

A Bluephase G2 multiple-peak LED (Ivoclar Vivadent, Schaan, Liechtenstein) with an 8.68-mm internal diameter tip was used in the current study. The output power (mW) was measured using a calibrated potentiometer (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel). Light irradiance (mW/cm^2) was determined by dividing the output power by the tip area. The spectral distribution was obtained using a calibrated spectrometer (USB2000, Ocean Optics, Dunedin, USA). Irradiance and spectral distribution data were integrated using an Origin 6.0 software program (OriginLab Northampton, MA, USA). A ceramic veneer specimen and a resin cement layer specimen were fixed to the tip of the multiple-peak LED to measure light attenuation (n = 5). The same analysis was also performed without the interposition of the ceramic and resin cement specimens, to provide a control group.[14]

Spectrophotometric absorption analyses

The absorption of each photoinitiator (CQ and TPO) in the 340-540 nm wavelength range was obtained by spectrophotometric analysis using a UV-Vis spectrophotometer (Thermo Scientific Evolution 201, Thermo Electron Scientific Instruments LLC, Madison, USA). Analysis was made by diluting 0.001 g of each photoinitiator in 1 mL of triethylene glycol dimethacrylate (Sigma-Aldrich, St. Louis, MO, USA). The spectra were collected using a quartz cell with a path length of 1 cm.[19]

Degree of conversion (DC)

Prior to sample preparation, 2 ml of primer was dispensed into a dark Eppendorf tube, and the solvent was evaporated using light air jets for 20 seconds, after which 2 ml of bond was added to the primer and mixed. The DC analysis was performed by making 10-mm-diameter by 1-mm-thick disc-shaped specimens of each adhesive system in rubber molds, followed by photoactivation (Bluephase G2 LED) for 20 s (n = 5). The light-curing was done with or without (control) the ceramic veneer (0.5 mm) and resin cement layers (0.3 mm) fixed on the output region of the light-curing tip. The specimens were evaluated immediately before and after polymerization, using a micro-Raman spectroscope (Xplora – Horiba Scientific, Tokyo, Japan) with a laser operating at 785 nm wavelength, 600-groove/mm diffraction grating, 300-µm pinhole aperture, and 100× objective. The absorption spectra of non-polymerized and polymerized experimental adhesives were recorded in a range from 1,500 cm^{-1} to 1,800 cm^{-1}, with an acquisition time of 10 s, and an average value of the recorded spectra obtained over three successive measurements at distinct points on the top face of the specimen. The DC calculations were performed by comparing the relative change in the aliphatic C=C peak at 1640 cm^{-1}, and the aromatic C=C peak at 1,608 cm^{-1}, using the following equation:

$$\text{DC (\%)} = 100 \times [1 - (\text{R polymerized} / \text{R non-polymerized})],$$

where R represents the ratio between the absorbance peak at 1,640 cm^{-1} and 1,608 cm^{-1}.

Cohesive strength (CS)

The samples for the CS analysis were prepared as described for the DC analysis (n = 10), but using rubber molds (Odeme, Luzerna, Brazil) with standardized dimensions (10 mm long x 3.5 mm wide x 1.5 mm thick in the constriction region). After preparation, the specimens were immediately transferred to a semi-universal test machine (Odeme - model OM-100, Luzerna, Brazil) and adapted to the tensile device for the CS test at a speed of 0.5 mm/min, with a load cell of 50N. The maximum load recorded for sample fracture was recorded in Newtons (N), and the CS was calculated in megapascals (MPa), using the following equation:

$$CS = F/A,$$

where F represents the tensile force (N), and A is the cross-sectional area of the sample in the constriction region (mm^2).

Microshear bond strength (*μ*SBS) test

Tooth selection and preparation

Fifty healthy human molars, extracted from patients for clinical reasons, were obtained. The inclusion criteria were teeth free from caries, restorations, cracks, or any other pathology. The teeth were stored in 0.5% chloramine T solution for seven days. The local research ethics committee reviewed and approved the protocol for this study (CAAE: 80918317.5.0000.5418).

The roots of the teeth were removed using the diamond disc of a cutting machine (Isomet 1000, Buehler, Lake Bluff, USA). Afterwards, the crowns were positioned on the cutting machine and sectioned to obtain four quarters: buccal, lingual, mesial, and distal (n = 200). These quarters were embedded in acrylic resin (Z-10 Acrylic Resin. Henry Schein, Melville, USA) using polyvinyl chloride tubes with a 25 mm diameter, and with the enamel surface facing the external region. Then, the specimens were abraded using 400-grit silicon carbide abrasive paper (APL 4, Arotec, Cotia, Brazil) to remove the enamel, and obtain a flat dentin surface. Immediately before initiating the restorative procedures, the dentin surfaces were wet-polished using 600-grit silicon carbide abrasive paper to standardize the smear layer.

Application technique of etch-and-rinse adhesives

Half of the embedded dentin quarters were restored using etch-and-rinse adhesive systems (n = 100), which were divided into 5 groups (n=20), according to the photoinitiator system used (CQ-only; 3CQ:1TPO; 1CQ:1TPO; 1CQ:3TPO; TPO-only). The dentin surface was etched with 37% phosphoric acid gel (Condac 37 - FGM, Joinville, SC, Brazil) for 15 seconds, rinsed for the same amount of time, and dried with absorbent paper. One coat of primer was applied for 20 s using vigorous agitation, followed by a gentle air jet for 5 s to evaporate the solvent. One coat of the adhesive was then applied. Half of each group was light-cured immediately using the multiple-peak LED for 20 s, as a control (n = 10). The other half was light-cured with resin cement photoactivation (n = 10).

Application technique of self-etch adhesives

The remaining dentin quarters were restored using self-etch adhesive systems (n = 100). The specimens were divided into 5 groups (n = 20), according to the photoinitiator system used (CQ-only; 3CQ:1TPO; 1CQ:1TPO; 1CQ:3TPO; TPO-only). One coat of primer was actively applied for 20 s, followed by a gentle air jet for 5 s to evaporate the solvent, and one coat of the adhesive was applied. Half of each group was light-cured immediately using the multiple-peak LED for 20 s, as a control (n = 10). The other half was light-cured by resin cement photoactivation (n = 10).

Resin cement specimen preparation

Tygon tubes (0.7mm internal diameter x 0.3 mm high) – two per dentin quarter – were positioned on the dentin surface and used as molds. The same resin cement (Variolink Esthetic LC, Ivoclar Vivadent, Schaan, Liechtenstein) was inserted into the tube using an exploratory probe. Light-curing was performed for 20 s on the ceramic veneer (0.5 mm), fixed on the output region of the light-curing tip. The specimens were stored for 24 h at 37°C, and at 100% relative humidity. The Tygon tubes were removed using a scalpel blade to expose the resin cement cylinders.

*μ*SBS test

The μSBS test was performed using a universal testing machine (Instron, model 4411, London, England). Each specimen was positioned in a metal device on the machine, and a thin stainless steel wire (0.2 mm in diameter) was looped around the base of each cylinder. The wire was aligned with the bonding interface and submitted to a crosshead speed of 0.5 mm/min, and a load cell of 50N, until failure. The mean of two cylinders of each dentin quarter was considered as the mean of that dentin quarter (n = 10) for statistical analysis.

Fracture analysis

The failure mode of the specimens was observed under an optical microscope (Leika Microsystems, Wetzar, Germany) at 40x magnification. The failure mode was classified as: adhesive, cohesive in dentin, cohesive in resin cement and mixed (involving dentin/adhesive/resin cement). Representative specimens of most of the frequent failure modes were mounted on aluminum stubs, and sputter coated with gold (Balzers SCD 050 Sputter Coater, Balzers Union, Balzers, Liechtenstein) to analyze the fracture patterns using scanning electron microscopy (SEM - JSM 5600 LV, JEOL, Tokyo, Japan).

Statistical analysis

The data were subjected to the Shapiro-Wilk test, and DC, CS and µSBS were analyzed using three-way ANOVA and Tukey's test ($p = 0.05$). The three factors analyzed were the thickness (ceramic + resin cement and control group), the photoinitiator system (CQ-only; 3CQ:1TPO; 1CQ:1TPO; 1CQ:3TPO; TPO-only) and the adhesive system (etch-and-rinse and self-etch). As for µSBS testing, the pre-test failures were included in the statistical analysis as zero results.

Results

Light transmittance

Figure 1 illustrates the emission peak within the blue spectrum at 460 nm, and a peak within the violet region at 410 nm for the multiple-peak LED. The irradiance was attenuated when the ceramic veneer and the resin cement layers were interposed, as confirmed by the reduction of both emission peaks.

Table 3 shows a reduction in the irradiance of blue and violet light through the ceramic and resin

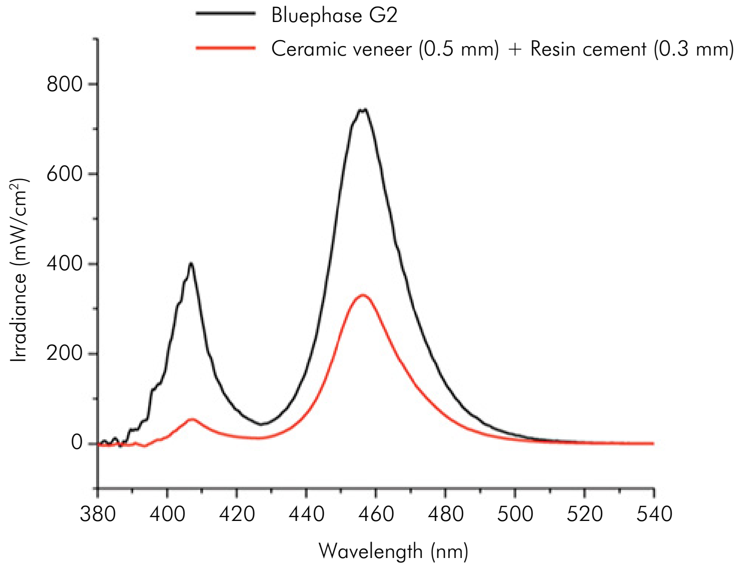

Figure 1. Spectral irradiance for multiwave LED, and irradiance attenuated by the interposition of the ceramic veneer and resin cement layers

Table 3. Light irradiance (mW/cm^2) transmittance (%) and attenuation (%) through ceramic veneer and resin cement.

Variable	Irradiance (mW/cm^2)			
	Bluephase G2	Ceramic 0.5 mm + Resin cement 0.3 mm	Transmittance (%)	Attenuation (%)
Violet - 380nm - 420nm	304.46	34.67	11	89
Blue - 420nm - 495nm	1096.35	467.46	43	57
Violet + Blue (total irradiance)	1397.18	502.07	36	64

cement. The transmittance within the violet spectrum was lower than that of the blue spectrum.

Absorption spectrophotometry

Figure 2 shows the absorbance of CQ and TPO. CQ absorbed light within the blue spectrum, with an absorption peak at 468 nm, thus overlapping the emission peak in the blue light region of the multiple-peak LED. TPO absorbed light near the UV-A region and extended out to the violet spectrum, with an absorption peak at 380 nm, overlapping the emission peak of the multiple-peak LED in the violet range.

Degree of conversion (DC)

Figure 3 shows similar DC values for all the adhesive systems in the control group. A decrease in DC through the ceramic veneer + resin cement layers was observed for the groups containing TPO at 75% and 100%. The lowest DC values were observed for the TPO-only adhesives. TPO up to 50% showed values similar to the CQ-only adhesive system and the control group. The analysis of variance (ANOVA) of the DC data showed that the "thickness" (p = 0.0001) and "photoinitiator" factors (p = 0.0001) were significant. The interaction between the "photoinitiator" and "thickness" factors was also significant (p = 0.0001). On the other hand, the "adhesive system" factor (p = 0.885) and the interactions between "adhesive system" and "photoinitiator" (p = 0.916); "adhesive system" and "thickness" (p = 0.974); and among "adhesive system," "thickness," and "photoinitiator" (p = 0.942) were not significant.

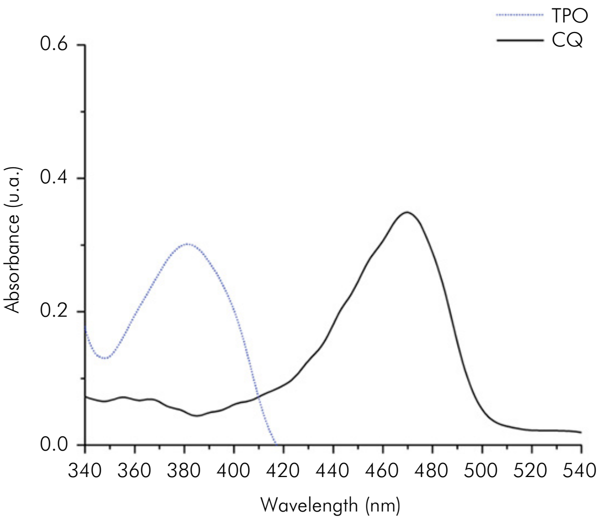

Figure 2. Camphorquinone (CQ) and diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO) in the 340-540 nm spectra

Cohesive strength (CS)

Figure 4 shows similar values for the CS in all the adhesive systems, when the ceramic veneer and resin cement layers were not interposed. The interposition of ceramic and resin cement reduced the CS of the adhesive systems containing 75% TPO. The adhesive system containing only TPO photoactivated through the ceramic veneer and resin cement showed the lowest CS means. The "photoinitiator" (p = 0.0001) and "thickness" (p = 0.0001) factors showed a significant effect on the CS values. The interaction between "photoinitiator" and "thickness" was also significant (p = 0.001). However, the "adhesive system" factor was not significant (p = 0.243), and the interactions between "adhesive system" and "photoinitiator" (p = 0.344); "adhesive system" and "thickness" (p = 0.980); and among these three factors (p = 0.774) were not significant.

Microshear bond strength (μSBS) test

Tables 5 and 6 show the microshear bond strength (μSBS), standard deviation, total number of specimens, and number of pre-test failures for all the adhesive systems, photoactivated with or without ceramic veneer and resin cement interposition. All the adhesive systems presented similar values in the control group, regardless of the photoinitiator system used. However, when the ceramic and resin cement were interposed, there was a reduction in all of their values. The adhesive system with TPO starting at 50% showed lower bond strength values than the adhesives with less TPO. The three-way ANOVA for μSBS data demonstrated that the "photoinitiator" (p = 0.0001) and the "thickness" (p = 0.0001) factors were significant, as was the interaction between "photoinitiator" and "thickness" (p = 0.0001). The "adhesive system" (p = 0.546) factor, and the interactions between "adhesive system"

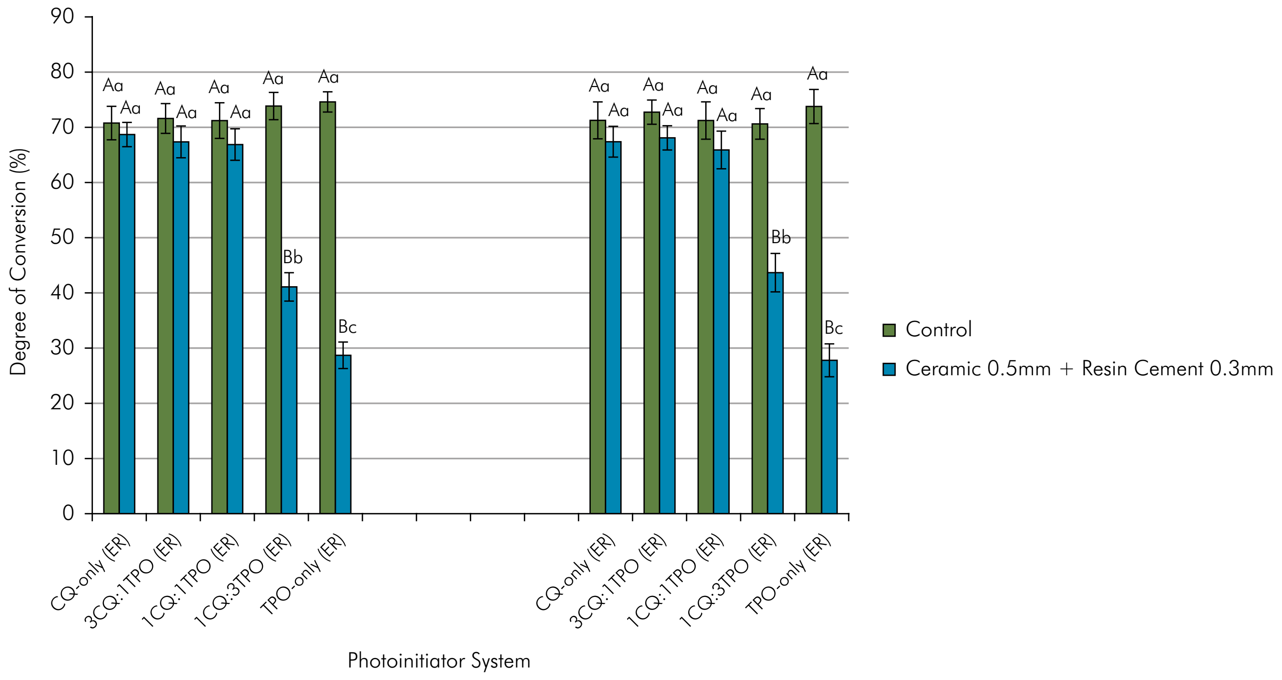

Figure 3. Degree of conversion of the tested experimental adhesives with different photoinitiator systems photoactivated through the ceramic veneer and resin cement layers

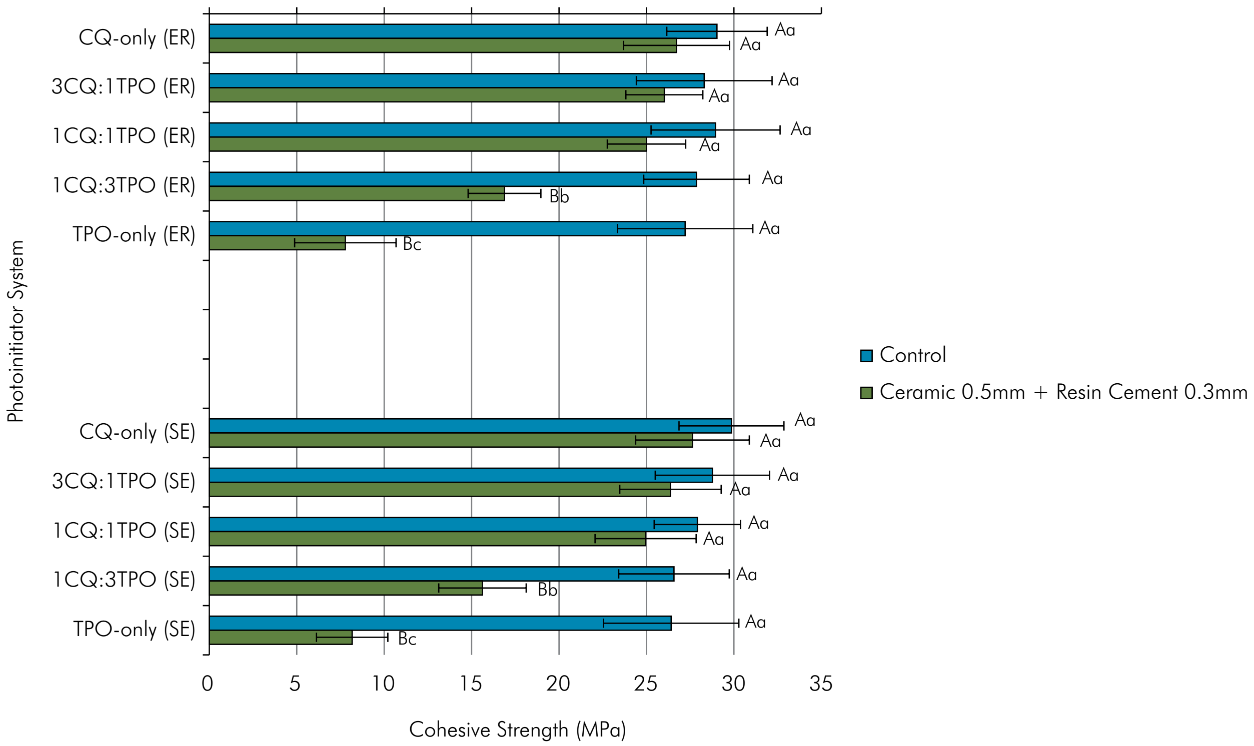

Figure 4. Cohesive strength for the tested experimental adhesives with different photoinitiator systems, photoactivated through ceramic veneer and resin cement layer

and "photoinitiator" (p = 0.187); "adhesive system" and "thickness" (p = 0.092); and among "adhesive system," "thickness," and "photoinitiator" (p = 0.812) were not significant.

Fracture analysis

Figure 5 shows that all the groups without interposed ceramic and resin cement showed predominately mixed failures. The adhesives that contained 75% and 100% TPO, and that were photoactivated through the ceramic and resin cement had a greater predominance of adhesive failures. Cohesive failures within resin cement were observed only in some control groups containing up to 50% CQ. No cohesive failures within dentin were observed.

SEM micrographs

Figure 6 shows SEM micrographs of debonded specimens. Images A and B show mixed failure for an etch-and-rinse adhesive with 1CQ:1TPO light-cured through the ceramic and resin cement layer, with remnants of the adhesive (a) and resin composite (c) attached to dentin (d). Images C and D show adhesive failure for an etch-and-rinse adhesive with 1CQ:3TPO, light-cured through the ceramic and resin cement layer. The exposed dentin and the presence of adhesive remnants in dentin tubules can be observed.

Figure 7 shows SEM micrographs of debonded specimens. Images A and B show mixed failure for a self-etch adhesive with 1CQ:1TPO light-cured through the ceramic and resin cement layer, with remnants of resin composite (c) attached to dentin (d). Images C and D show adhesive failure for a self-etch adhesive with 1CQ:3TPO light-cured through the ceramic and resin cement, with exposure of dentin and the presence of adhesive remnants in dentin tubules.

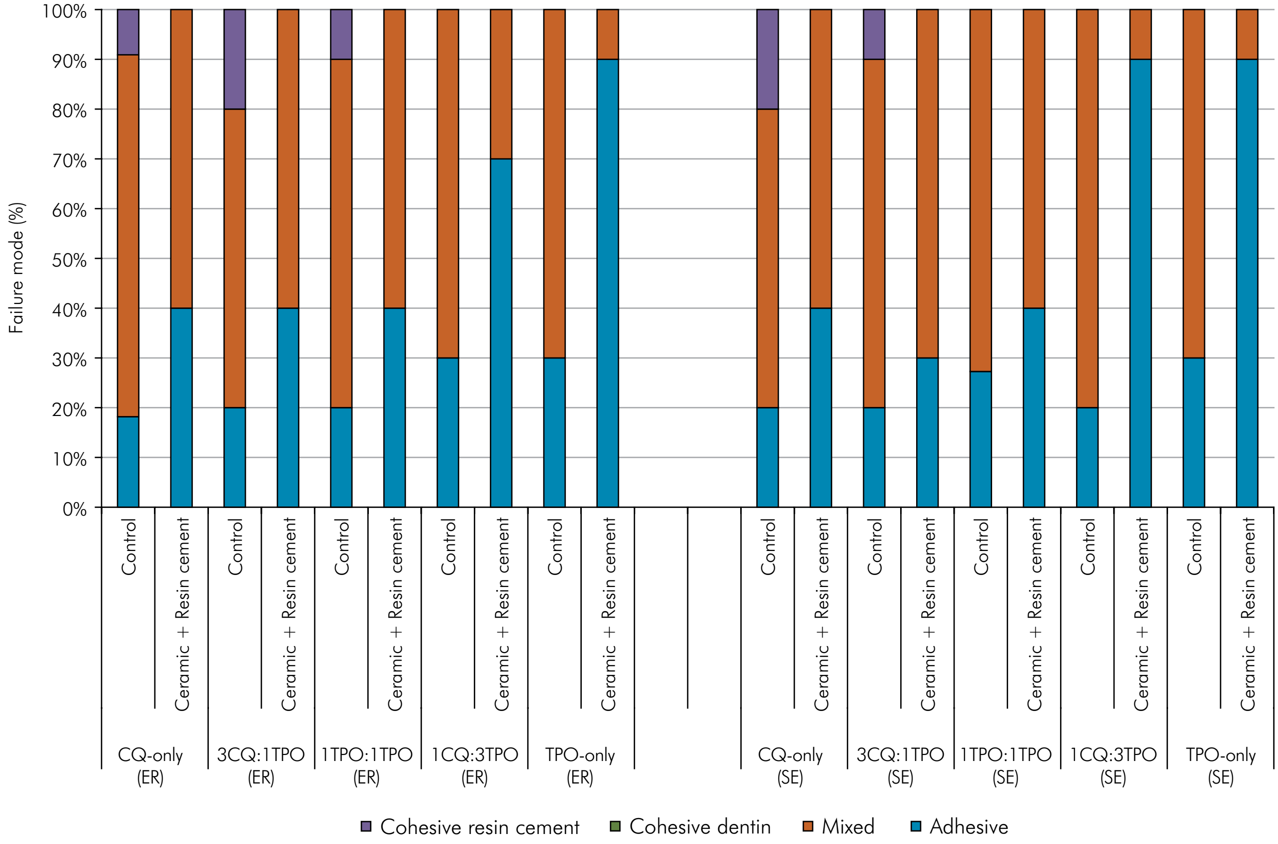

Figure 5. Failure mode analysis of debonded specimens (%)

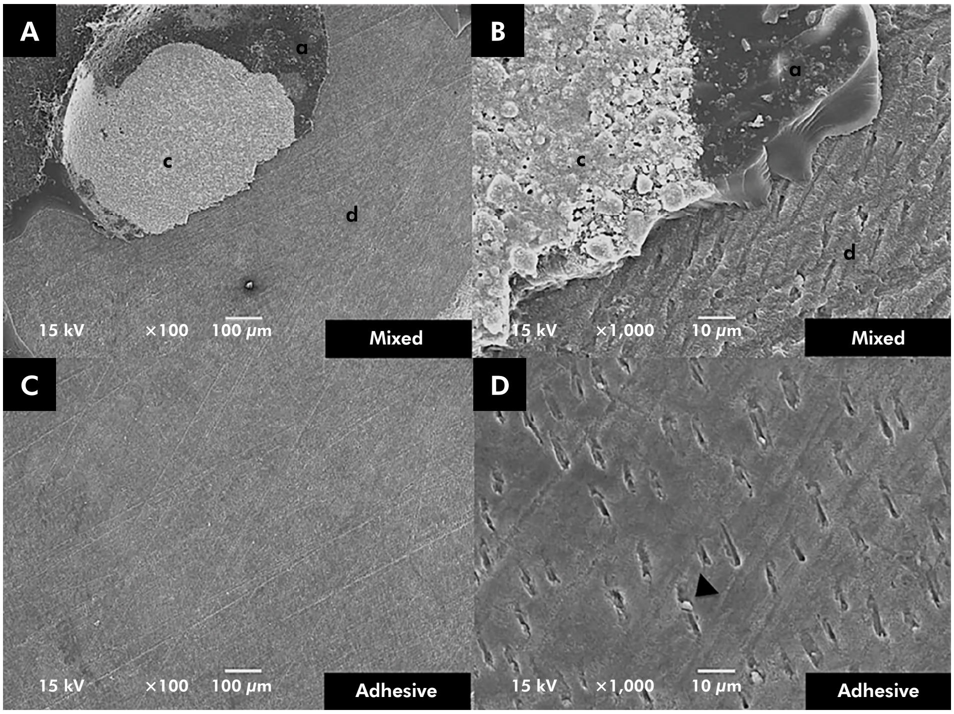

Figure 6. SEM micrographs of debonded specimens of etch-and-rinse adhesive system. Images A and B (1CQ:1TPO) show mixed failure, with remnants of adhesive (a) and resin composite (c) attached to dentin (d). Images C and D (1CQ:3TPO) show adhesive failure with adhesive remnants in the dentin tubules.

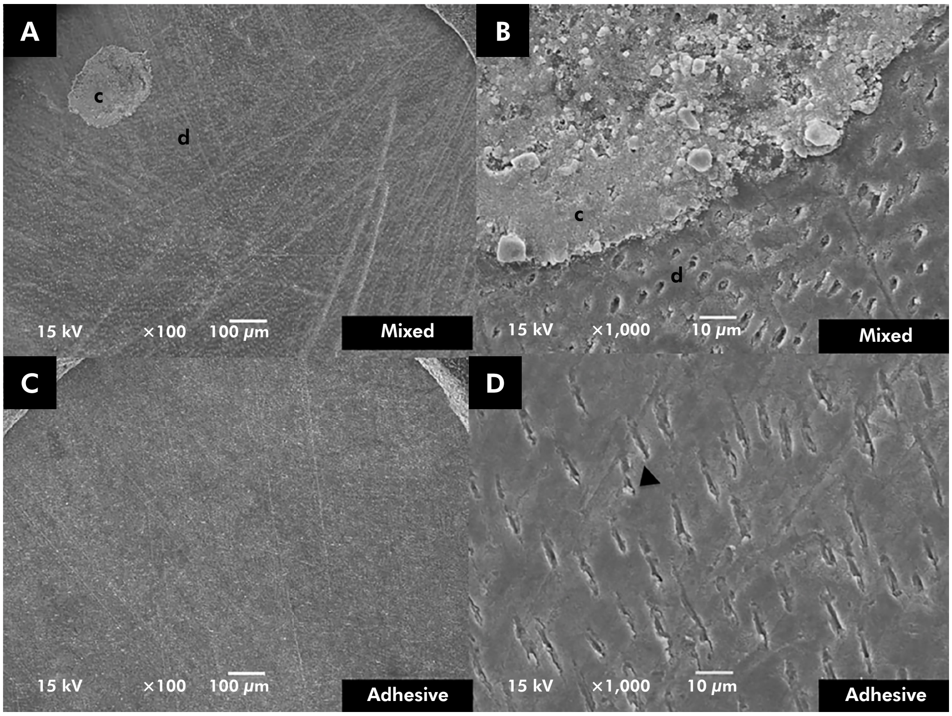

Figure 7. SEM micrographs of SE adhesive system debonded specimens. Images A and B (1CQ:1TPO) show mixed failure, with remnants of resin composite (c) attached to dentin (d). Images C and D (1CQ:3TPO) show adhesive failure with dentin tubules containing adhesive remnants.

Discussion

The first research hypothesis – that the interposition of ceramic veneer and resin cement layers would influence light transmittance to the adhesive layer – was accepted. As seen in Figure 1, despite the high irradiance of the multiple-peak LED, most of the light is emitted in the blue spectrum, and only a small portion in the violet range, approximately 22%. Additionally, there was a marked attenuation of the total irradiance emitted when the ceramic veneer and resin cement were interposed, mainly in the violet spectrum. Table 3 shows that only 11% of the violet light emitted reached the adhesive layer; this poses a problem for photoinitiators that absorb light in this wavelength range.

There are several factors that interfere with the transmission of light through materials, including light irradiance, exposure time, material shade, translucency and material composition.[17] In this study, the IPS Empress Esthetic ceramic had 35 ± 5 vol% of leucite crystals – a greater number of crystals leads to greater light scattering, and less absorption of the light by the material.[20] Thus, less light transmission is expected through reinforced glass ceramic than feldspathic ceramic.[21,22] In addition to the composition of the ceramic, it is important to consider the refractive index, according to which less light scattering is found when there are smaller differences between the refractive indexes of the material components. The reason for this is the reduction in reflections and refractions at the interfaces of these components, hence greater light transmittance.[20] Leucite crystals have a similar refractive index to the glassy matrix, 1.51 and 1.50 respectively;[20] therefore, this material is expected to have high transmittance. However, the scattering effect might occur when the size of the crystal is approximately half of or similar to the incident light wavelength.[20] Another factor that could influence this property is the presence of porosities in the glass,[20] because the lower refractive index of the pore (about 1.0)[23] leads to light scattering.

The manufacturer of Variolink Esthetic LC describes a similar refractive index between the resin matrix and filler particles.[24] However, the filler size also has to be considered, and the manufacturer states that the filler particles range in size from 100 to 200 nm. According to the Rayleigh scattering theory, in order for the light to be scattered by a particle, the particle size must be similar or smaller than the wavelength radiation.[25] In other words, greater light scattering occurs when the composite filler particles have a diameter smaller than or close to the value of the irradiated wavelength. The resin cement used in this study had a filler size smaller than the wavelength value of the incoming light of the multiple-peak LED (approximately 385-515 nm), inferring that the resin cement also had an effect on light scattering.

Light attenuation may influence the mechanical properties of indirect restorations; however, the absorption capacity of the photoinitiator systems also has to be taken into account. As observed in Figure 2, TPO absorbs light only in the violet spectrum, whereas CQ absorbs light in the blue range. Thus, it was expected that TPO would present a lower degree of conversion than CQ, since the amount of attenuated violet light was much greater than that of attenuated blue light. As observed in Figure 3, the DC was similar among the photoinitiator systems in the control groups, regardless of the differences in CQ and TPO ratios. Previous studies also observed similar DC values among resin materials with TPO-only, CQ-only/amine or a combination of these two initiators.[8,19,26] The high light absorption of TPO exposed to a violet light source is attributed to its high efficiency in free radical formation and efficient quantum yields.[7] When the TPO photoinitiator is activated by incoming photons, the photochemical process triggers the cleavage of the C–P bond of the molecule, forming two radicals that can diffuse through the resin medium and immediately initiate polymerization.[10] Unlike TPO activation, the CQ molecule shifts to an excited state after absorbing light, and interacts with a hydrogen-donating co-initiator, usually an amine-derivate. Although free radicals can indeed be formed, the velocity of radical formation depends on the proximity of the CQ to the amine. In this case, only one active free-radical is expected to initiate polymerization.[10,19]

The DC can be an indicator of the quality of a polymer,[27] considering that a greater DC could imply an improvement in the mechanical properties of the polymer.[28] Accordingly, the control groups and the groups with up to 50% TPO recorded the highest DC values (Figure 3), and also were the groups with the highest CS (Figure 4) and μSBS values (Tables 4 and 5). However, as the violet light was very attenuated from the interposition of ceramic veneer and resin cement, the polymerization and mechanical properties of the adhesives containing high concentrations of TPO (75 and 100%) were affected. Thus, the second hypothesis -- that the interposition of ceramic veneer and resin cement layers would affect the cure efficiency and mechanical properties of the adhesive system layer – was accepted. Previous studies have also observed that light attenuation can affect the mechanical properties of resin materials.[11,12,14]

The adhesive systems containing TPO-only showed the lowest DC, CS, and μSBS values under the ceramic veneer and resin cement layers. Thus, the third hypothesis -- that the use of different photoinitiator systems would affect the cure efficiency, cohesive strength, and bond strength – was also accepted. When the ceramic veneer and resin cement layers were interposed, the combination of CQ and TPO had higher cure efficiency and mechanical properties than TPO-only. The best concentration of TPO was up to 50% of the total amount of photoinitiator, because the values were similar to the control groups and greater than the groups containing TPO at 75% and 100%, when the ceramic and resin cement were interposed. This proves that the difference in attenuation at the different wavelength spectra, in which each photoinitiator absorbs light directly, influences the adhesive performance. However, it is important to consider that the reduced irradiance and transmittance of violet light factors were important factors to obtain these results.

The amount of absorbed blue light helped compensate for the low absorption of violet light by TPO under the ceramic and resin cement layers, when CQ and TPO were combined, at concentrations at or above 50% for CQ. Thus, there was a higher DC of the adhesive system, hence improvement in all mechanical properties. A previous study evaluated the curing efficiency of resin composites containing a combination of CQ and TPO; it observed that the greater the amount of TPO in relation to CQ, the lower the cure efficiency in deeper regions of the restoration.[12] Although a low degree of conversion adversely affects the mechanical properties of the materials, it can also increase the leaching of the unreacted monomers.[9] Studies have shown that unpolymerized TEGDMA and HEMA used in non-toxic concentrations undergo saponification by enzymatic hydrolysis, which breaks down these molecules into molecules of methacrylic acid. This

Table 4. Microshear bond strength means (± standard deviation) for ER experimental adhesive systems with and without interposed ceramic veneer and resin cement layer

Photoinitiator system	Microshear bond strength (MPa)	
	Control	Ceramic + resin cement
CQ-only (ER)	27.28 ± 2.15 Aa (0/20)	22.05 ± 2.08 Ba (0/20)
3CQ: 1TPO (ER)	28.07 ± 3.50 Aa (0/20)	20.09 ± 3.11 Ba (0/20)
1CQ:1TPO (ER)	27.27 ± 2.46 Aa (0/20)	19.23 ± 2.62 Ba (0/20)
1CQ:3TPO (ER)	25.23 ± 2.90 Aa (0/20)	11.19 ± 5.88 Bb (4/16)*
TPO-only (ER)	26.51 ± 2.67 Aa (0/20)	6.26 ± 4.40 Bc (6/14)*

Different uppercase letters in rows and lowercase letters in columns indicate statistically significant difference ($p < 0.05$); *Number of pre-testing failures per total number of micro-specimens is mentioned.

Table 5. Microshear bond strength means (± standard deviation) for SE experimental adhesive systems with and without interposed ceramic veneer and resin cement layer.

Photoinitiator system	Microshear bond strength (MPa)	
	Control	Ceramic + resin cement
CQ-only (SE)	27.53 ± 2.64 Aa (0/10)	21.45 ± 2.57 Ba (0/10)
3CQ: 1TPO (SE)	26.75 ± 2.70 Aa (0/10)	20.99 ± 2.08 Ba (0/10)
1CQ:1TPO (SE)	27.80 ± 2.49 Aa (0/10)	20.06 ± 2.06 Ba (0/10)
1CQ:3TPO (SE)	26.41 ± 2.47 Aa (0/10)	9.30 ± 6.41 Bb (2/8)*
TPO-only (SE)	26.90 ± 2.48 Aa (0/10)	5.08 ± 3.71 Bc (4/6)*

Different uppercase letters in rows and lowercases letter in columns indicate statistically significant difference ($p < 0.05$); *Number of pre-test failures per total number of micro-specimens is mentioned.

increases the toxicity and the adverse side effects of dental materials, because these molecules can be leached into saliva, reach the gastrointestinal tract, and alter cell function.[29,30]

Tables 4 and 5 show reductions in bond strength for all the groups when ceramic veneer and resin cement were interposed, unlike the results observed for DC and CS. This could be attributed to the photoactivation of the specimens for the microshear bond strength test through the ceramic veneer and unpolymerized resin cement, in order to simulate a clinical situation. These results were different from those for DC and CS, in which pre-polymerized resin cement was interposed. Interposition could have affected the light transmittance, owing to a possible resin-filler refractive index mismatch. Some aspects, such as resin matrix composition and filler morphology, which includes size and distribution, might effect a change in the refractive index of the polymers formed, which become similar to the filler particles.[31] This change is partly due to the enhanced density of the polymer, compared with the monomer, as well as to the decrease in molecular mobility as the cross-linking density and the viscosity increase.[32] However, the refractive index of the methacrylate monomers is usually lower than that of the filler particles prior to polymerization. This could lead to greater light scattering in the microshear bond strength specimens than that caused by a pre-polymerized resin cement, as observed in the other tests.[33,31]

It is important to emphasize that the color of the restorative materials and the irradiance were standardized in the present study. However, light transport is limited by the opacity of the indirect materials, which results in less conversion or lower mechanical properties of resinous materials.[34] Thus, the curing parameters of power and irradiation time must be reevaluated according to different combinations of materials, shades and light-curing units, in order to reach an optimal DC.

As can be seen in Figure 5, the mixed failure mode was predominant in the control groups, and resulted from higher microshear bond strength values. However, the interposition of ceramic veneer and resin cement led to an increase in the percentage of adhesive failures, mainly in adhesive systems containing more than 50% TPO. This occurred because light attenuation was higher in the violet spectrum through the ceramic and resin cement; therefore, TPO received lower energy and was not able to trigger adequate polymerization. Another possibility is that polymers were formed with deficient mechanical properties, leading to lower bonding values. The more frequently observed failure modes for the adhesive systems are shown in the SEM micrographs in Figure 6 and Figure 7.

Regarding the etch-and-rinse and self-etch modes, these adhesive systems had similar bond strengths, with no statistical differences, regardless of the other factors evaluated. This could be attributed to the similar composition of the monomers contained in both systems. The only difference was the GDMA monomer used in the etch-and-rinse adhesive, and the GDMA-P used in the self-etch adhesive systems. A previous study evaluated the behavior of GDMA in etch-and-rinse and self-etch adhesives, and observed similar values among them for DC and bond strength after 6 months. These results were better than those of adhesives containing HEMA.[35] The concentration of GDMA-P in self-etching adhesives was evaluated previously, and adhesives containing 15% GDMA-P in their formulation were found to have satisfactory immediate bond strength (41.8 MPa).[36]

Total replacement of CQ by TPO in simplified adhesive systems can improve their cure efficiency and hydrophilicity.[3,37] However, the use of TPO-only in adhesive systems did not prove effective for indirect restorations in this study, because of their low energy absorption under the restorative materials. Thus, polymers with poor mechanical properties were obtained. Replacing CQ with up to 50% TPO in dental adhesives proved to be a good alternative, since it promoted similar or improved DC, CS, and bond strength over TPO-only adhesives. However, this group (up to 50% TPO) did not show any benefits in DC, CS or bond strength in the short-term. In this sense, future studies should evaluate the long-term bond strength to determine whether the same findings remain valid over time. It would also be interesting to evaluate if the combination of CQ and TPO in a 1:1 ratio would be sufficient to improve water compatibility and co-polymerization of hydrophilic monomers, and avoid phase separation at the micro or nano level in simplified adhesives.

Conclusion

Under the conditions of this study, it can be concluded that:

a. The violet spectrum is more intensely affected by light attenuation through ceramic veneer and resin cement. This attenuation directly affected the degree of conversion and mechanical properties of etch-and-rinse and self-etch adhesives containing high concentrations of TPO.
b. The addition of up to 50% TPO in combinations with CQ in adhesive systems, when photoactivated with the interposition of the restorative materials, had degree of conversion, cohesive strength, and microshear bond strength results similar to those of the control groups.

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