Evaluation of degree of conversion and the effect of thermal aging on the color stability of resin cements and flowable composite

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Abstract

**Purpose:** The aim of this in vitro study was to evaluate the color stability and degree of conversion (DC) of dual-cure and light-cure cements and flowable composites after thermal aging.

**Materials and Methods:** A total of 50 human incisors were prepared and divided into six groups \((n=10)\). Veneers were fabricated using IPS Empress Direct composite resin were bonded with three types of luting agents: Light-cured, conventional dual, and flowable composite according to the manufacturer’s instructions. The groups were as follows: Filtek Z350XT Flow/Single Bond 2, RelyX ARC/Single Bond 2, RelyX Veneer/Single Bond 2, Tetric N-Flow/Tetric N-Bond, and Variolink II/Tetric N-Bond. Commission Internationale de l’Éclairage \(L^*, a^* \text{ and } b^*\) color coordinates were measured 24 h after cementation procedure with a color spectrophotometer and reevaluated after 10,000 thermal cycles. To evaluate the DC 50 specimens \((n=10)\) of each resin material were obtained and Fourier transform infrared spectroscopy was used to evaluate the absorption spectra. Statistical analysis was performed with one-way ANOVA and Tukey’s test \((\alpha = 0.05)\).

**Results:** No statistically significant differences in \(\Delta E^*\) occurred after aging. The greatest change in lightness occurred in the Variolink II resin cement. Changes in red–green hue were very small for the same cement and largest in the Tetric N-Flow flowable resin composite, while the greatest change in blue–yellow hue was a yellowing of the RelyX ARC luting cement. RelyX ARC exhibited the highest DC, and there were no statistically significant differences in DC among the other cements.

**Conclusions:** Resin-based luting agent might affect the final of ceramic veneer restorations. The thermal aging affected the final color of the evaluated materials, and these were regarded as clinically unacceptable \((\Delta E >3.3)\).

**Keywords:** Color; degree of conversion; resin cements

INTRODUCTION

All-ceramic crowns and laminate veneers are the most common restorations in the anterior region due to their esthetic and natural appearance.¹ However, the properties of laminate veneers, such as compatibility with the periodontal tissues, clinical longevity, surface texture and more conservative approach compared with all-ceramic restorations,² make them an excellent choice.³ These materials are used to close diastemas, restore morphological and structural defects, and improve the appearance of mildly discolored teeth.⁴

The success of treatment depends on the perfect association of colors between the indirect restorations and remaining...
teeth,[5] and there are many factors involved, for example, the color of the tooth structure,[6] thickness, type and shade of ceramic,[7] and the luting systems.[8] The currently available resin cements specifically used for laminate veneers cementation procedure are usually activated by visible light.[9] The main advantages of these materials are their great color stability and longer working time when compared to chemically and dual-cured systems,[10] which makes it easier to remove the excess, thus reducing cementation time.[11] Furthermore, they do not use amine as a chemical initiator, which may cause color changes over the long-time.[12]

To associate some of the advantageous characteristics of chemically and light-cured cements, dual-cured systems have been developed.[13] Such materials have superior mechanical properties, such as flexural strength, hardness, and degree of conversion (DC) in comparison to the isolated light activation or chemical activated.[14] The chemical-cured component is expected to ensure complete polymerization in deeper areas where light is attenuated.[15] However, dual-cured systems contain aromatic tertiary amine in their composition, which might cause color changes in the cement over time.[12] The color stability commitment is usually associated with the oxidization of the unreacted amine co-initiator from the redox polymerization system. The presence of unreacted benzoyl peroxide in dual-polymerizing agents may also lead to greater color instability, which would jeopardize the long-term esthetic appearance of the restoration.[15] For this reason, some authors have suggested luting laminate veneers with flowable resin composites.[9] These materials were developed in 1996 and present the same particle size as a hybrid composite but produce a reduction in the viscosity.[9] Flowable composite resins are less expensive than resin-based cements and maximize the range of shades available.[15]

Several studies have shown that some factors such as type, thickness and color of the ceramic,[16] as well as the type of curing mode,[17] can affect the complete polymerization. A higher DC[18] results in improved physico-chemical properties and is clinically related to a decrease in marginal wear,[19] increased biocompatibility,[20] and decreased color stability.[21] Several methodologies have been developed to analyze the DC in the organic matrices of bisphenol-A glycidyl dimethacrylate (BIS-GMA)-based resin composites, most of which employ Fourier transform infrared spectroscopy (FTIR).[9]

Based on such information, the purpose of this in vitro study was to evaluate color stability and DC of dual-cure and light-cure cements and flowable resin composites in the dental substrate after thermal aging. The hypotheses tested in this study were as follows: (1) Light-cured cements are more stable than other luting systems after thermal aging and (2) the color stability and DC of flowable resin composites used as cements is similar to dual-cure and light-cure cements after thermal aging.

MATERIALS AND METHODS

Specimen preparation

For this experiment, 50 human upper central incisors were selected, cleaned, and stored in 0.5% chloramine-T solution at 4°C. The thickness of the facial surfaces of the teeth were reduced in 0.6 mm by using a high-speed diamond bur #2135 (KG Sorensen) under air-water cooling on a standard preparation device. The burs were replaced after every five preparations. Impressions were obtained by using a polyether impression material (Impregum F, 3M/ESPE, Seefeld, Germany) and plaster models were prepared by using special type IV plaster. Veneers were fabricated with IPS Empress Direct composite resin and underwent light curing with a light-emitting diode-curing unit for 40 s and then put in an FDG-LUX oven to complete the curing for 3 min. Following this, a mono-component silane (Monobond S Ivoclar Vivadent) was applied and left undisturbed for 1 min before the application of the adhesive system.

The prepared teeth were randomly divided into five experimental groups (n = 10), according to the used type of luting system: G1-Rely X Veneer/Single Bond 2 (RV/SB), G2-Rely X ARC/Single Bond 2 (RA/SB), G3-Filtek Z350 XT Flow/Single Bond 2 (XT/SB), G4-Variolink II/Tetric N-Bond (VI/TB), and G5-Tetric N-flow/Tetric N-bond (TF/TB). The enamel surface of all samples was etched with 35% phosphoric acid gel (Scotchbond, 3M ESPE, St. Paul, MN) for 15 s, which was followed by washing and removal of excess with absorbent paper. Then, bonding procedures for luting were executed as follows.

Group 1 (RV/SB)
The adhesive (SB) was prepared and handled in accordance with the manufacturer’s instructions. The solvent was evaporated by using a gentle air stream for 5 s. A layer of adhesive was applied, followed by the luting cement directly onto the veneer. Veneer was inserted, followed by light polymerization with a light-curing unit for 40 s.

Group 2 (RA/SB)
The adhesive (SB) was prepared and handled in accordance with the manufacturer’s instructions. The solvent was evaporated using a gentle air stream for 5 s. A layer of adhesive was applied directly onto the veneer. For RelyX ARC, equal amounts of base and catalyst pastes were mixed for 10 s. The veneer was then inserted and pressed, followed by light polymerization with a light-curing unit for 40 s.
**Group 3 (XT/SB)**
The adhesive (SB) was prepared and handled in accordance with the manufacturer’s instructions. The solvent was evaporated using a gentle air stream for 5 s. For Filtek Z350 XT Flow, the resin was applied; the veneer was inserted and pressed, followed by light polymerization with a light-curing unit for 40 s.

**Group 4 (VII/TB)**
The adhesive (TB) was prepared and handled in accordance with the manufacturer’s instructions. The solvent was evaporated using a gentle air stream for 5 s. For the Variolink II cement, equal amounts of base and catalyst pastes were mixed for 10 s, the veneer was inserted and pressed, followed by light polymerization with a light-curing unit for 40 s.

**Group 5 (TF/TB)**
The adhesive (TB) was prepared and handled in accordance with the manufacturer’s instructions. The solvent was evaporated using a gentle air stream for 5 s. For Tetric N-Flow, the layer of adhesive was applied directly onto the veneer, the resin was applied, the veneer was inserted and pressed, followed by light polymerization with a light-curing unit for 40 s.

**Initial color measurements**
Color coordinates L*, A*, and b* were measured Commission Internationale de l’Éclairage (CIE) system, were measured with a spectrophotometer (Easyshade, VITA Zahnfabrik, BadSackingen, Germany). This pattern consists of two axes, a* and b*, which are at right angles are represent the shade or color dimension. The third axis, perpendicular to a* and b* plane, is the lightness L*.

The specimens were dried with absorbent paper, and placed on a light box (MM‑1eUV/D65). For color readout, the point was centralized and placed on the specimen that occupied its entire diameter, allowing readout in the same position at all times.

**Thermal aging**
Initial color readout was performed 24 h after cementation. After initial readings, all samples were submitted to 10,000 thermal cycles (MSCT – 3e ELQUIP, Sao Carlos, Brazil). Each thermal cycle consisted of alternated immersion in distilled water at 5 ± 1°C, 37 ± 1°C, and 55 ± 1°C for 30 s for each dwell time.

**Final color measurements**
After thermal aging, final color readouts were performed. Color alteration (ΔE) was calculated by the following formula: ΔE = ([ΔL]² + [Δa]² + [Δb]²)¹/², in which L* indicates the lightness, (from 0 = black up to 100 = white), a* indicates the green–red axis (from - a = green up to + a = red) and b* indicates the blue–yellow axis (from - b = blue up to + b = yellow). Values of ΔE* ≥3.3 were considered clinically unacceptable based on a previous study.[21]

**Degree of conversion**
Fifty specimens (n = 10) of each luting systems group (0.5-mm height and 5.0-mm diameter) were prepared. Luting systems were mixed according to the manufacture’s instructions.

DC% was measured after 24 h using an FTIR spectrometer (Spectrum 100, Perkin Elmer Corp, Norwalk, CT, USA) on the attenuated total reflectance-sampling accessory. The spectra were recorded from 650 to 4000/cm as the average of 32 scans at a resolution of 4/cm. DC was calculated from the aliphatic C = C peak at 1638/cm, normalized against the aromatic C = C peak at 1608/cm, in the uncured and cured forms according to the following formula: DC = 100 × (1-[C = C cured/aromatic cured]/[C = C uncured/aromatic uncured]).

**Statistical analysis**
The obtained data in the color stability and DC tests were submitted to the one-way ANOVA statistic test, and the measurements were compared by means of the Tukey test. All tests were performed with a significance level of 5%.

**RESULTS**

**Color stability**
The ΔE values for each group are presented in Table 1. There was no significant difference in color stability after thermal aging. Based on the analysis of changes in value or lightness (L*), the highest value was attributed to the Variolink II resin cement. Changes in red–green hue (a*) were very small for the same cement and largest in the Tetric N-Flow flowable resin composite, while the greatest change in blue–yellow hue (b*) was a yellowing of the RelyX ARC luting cement.

**Degree of conversion**
The results for DC are listed in Table 2. The RelyX ARC resin cement exhibited higher monomer polymer and conversion rate, with the statistically significant difference compared to the others luting systems.

**DISCUSSION**
Thermal cycling was employed to simulate long-term exposure to conditions within the oral cavity. Temperature and humidity are known to cause oxidation of amines, which are necessary components of adhesives for initiating polymerization,[22] but may cause color changes in cements during aging.
Table 1: Mean values for ΔL*, Δa*, Δb*, and ΔE* of luting cements (P<0.05). The coordinate L* represents the lightness, or black/white characteristics of the color. The a* coordinate yellow–blue axis and the b* coordinate red–green axis.

| Resin cement | ΔL*   | Δa*    | Δb*    | ΔE*   |
|--------------|-------|--------|--------|-------|
| Z350 XT flow | 77.3 (0.18)a | −0.09 (0.06)b | 14.66 (0.18)c | 5.5 (2.9)d |
| RelyX ARC    | 73.39 (0.20)a | −1.13 (0.07)c | 21.66 (0.41)a | 3.9 (1.4)a |
| RelyX veneer | 76.19 (0.63)c | −0.19 (0.11)c | 12.95 (1.20)d | 3.6 (4.3)c |
| Tetric N flow| 76.63 (0.85)c | 0.41 (0.20)a | 17.04 (0.70)d | 4.1 (2.2)c |
| Variolink II | 80.24 (0.24)a | −2.33 (0.07)c | 16.87 (0.84)a | 3.6 (2.1)c |

Groups identified using the same letters did not exhibit statistically significant differences (P<0.05).

Table 2: Mean degree of conversion of luting cements

| Resin cement | DC (%) |
|--------------|--------|
| RelyX ARC    | 68.4 (1.6)a |
| Z350 XT flow | 57.9 (4.3)c |
| RelyX veneer | 57.5 (3.2)c |
| Tetric N flow| 56.8 (1.9)c |
| Variolink II | 54.1 (2.6)c |

Different letters indicate significant statistical differences within luting systems. DC: Degree of conversion.

The first study hypothesis was that the light-cured cements are more stable than other luting systems after thermal aging. The results of the study have indicated that the hypothesis was not accepted because there were no significant differences in ΔE* for the luting systems. The aromatic tertiary amines used in dual-cured materials are more likely to oxidize than the aliphatic amines used in light-cured materials, while the light-cured cements were expected to exhibit better color stability.[22,23] However, all luting systems contained some type of amine in the form of accelerators and inhibitors.[24] Decomposition of inhibitors was found to cause a change to a yellowish hue.[25] The RelyX ARC resin cement exhibited the greatest b* value, possibly due to a greater concentration of oxidized amine or the yellow color of camphorquinone, another component.

The CIE L*a*b* system was developed by the CIE for describing the color characteristics of an object based on three parameters: Lightness–darkness (L*), red–green hue (a*), and yellow–blue hue (b*). The Variolink II resin cement possessed the highest values of L*, indicating that the cement was the lightest material following thermal aging. Tetric N Flow flowable resin exhibited the highest value for a* parameter, indicating that this material presents a red hue after aging.

The ΔE values of the luting systems were statistically similar. Several ΔE values have been proposed as a “clinically acceptable” color change value. Most studies have applied a value of ΔE ≥3.3[21] as the threshold for clinical acceptability. All resin cements evaluated in this study have experienced a color change of this magnitude.

The second hypothesis, according to which the color stability and DC of the flowable composites used as cements would be similar to the dual-cure and light-cure cements after thermal aging, was accepted. All groups have displayed similar behavior with respect to DC except for RelyX ARC cement, in which the DC was higher than the other luting systems, including two other materials from the same manufacturer (RelyX Veneer and Filtek Z350 XT Flowable) which contain the same type of filler particles (silica/zirconia) in similar concentration by weight (67.5%, 66%, and 65%).[9] However, the composition of the organic matrix of the flowable composite differs from the other materials since it contains bisphenol A ethoxylated dimethacrylate, as well as Bis-GMA and triethylene glycol dimethacrylate.[9] Such component may decrease the mechanical properties of the material because it is particularly sensitive to polymerization conditions. A previous study has reported better polymerization in dual-cured cements[25] such as RelyX ARC, adding that the improved performance may be because it is cured using both chemical and photonic mechanisms. However, additional simulated aging studies are necessary to examine the color stability of various luting systems and improve the esthetic longevity of indirect restorations.

CONCLUSIONS

- The thermal aging has led to color changes in all the evaluated materials; they were considered clinically unacceptable (ΔE >3.3).
- RelyX ARC has shown the highest DC values than the other materials tested.
- There were no statistically significant differences in DC among the other cements.

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Conflicts of interest

There are no conflicts of interest.

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