Colour stability and opacity of resin cements and flowable composites for ceramic veneer luting after accelerated ageing

Lucí Regina Panka Archegas\textsuperscript{a}, Andrea Freire\textsuperscript{b}, Sergio Vieira\textsuperscript{c}, Danilo Biazetto de Menezes Caldas\textsuperscript{d}, Evelise Machado Souza\textsuperscript{c,*}

\textsuperscript{a}Professional and Technological Education Center, Federal University of Parana, R. Dr. Alcides Vieira Arcoverde, 1225, 81520-260 Curitiba, PR, Brazil
\textsuperscript{b}School of Dentistry, Pontifical Catholic University of Parana, R. Imaculada Conceição, 1155, 80215-901 Curitiba, PR, Brazil
\textsuperscript{c}Graduation Program in Dentistry, School of Dentistry, Pontifical Catholic University of Parana, R. Imaculada Conceição, 1155, 80215-901 Curitiba, PR, Brazil
\textsuperscript{d}Esthetic Dentistry Based on Scientific Evidence, Continuing Education Course at the Brazilian Dental Association, Parana Section, R. Dias da Rocha Filho, 625, 80045-275 Curitiba, PR, Brazil

\textbf{A R T I C L E   I N F O}

Article history:
Received 7 June 2011
Received in revised form 20 August 2011
Accepted 25 August 2011

Keywords:
Resin cements
Flowable composites
Accelerated ageing
Colour stability
Opacity
Ceramic veneer

\textbf{A B S T R A C T}

Objectives: Colour changes of the luting material can become clinically visible affecting the aesthetic appearance of thin ceramic laminates. The aim of this in vitro study was to evaluate the colour stability and opacity of light- and dual-cured resin cements and flowable composites after accelerated ageing.

Methods: The luting agents were bonded (0.2 mm thick) to ceramic disks (0.75 mm thick) built with the pressed-ceramic IPS Aesthetic Empress (n = 7). Colour measurements were determined using a FTIR spectrophotometer before and after accelerated ageing in a weathering machine with a total energy of 150 kJ. Changes in colour (ΔE) and opacity (ΔO) were obtained using the CIE L*a*b* system. The results were submitted to one-way ANOVA, Tukey HSD test and Student’s t test (α = 5%).

Results: All the materials showed significant changes in colour and opacity. The ΔE of the materials ranged from 0.41 to 2.40. The highest colour changes were attributed to RelyX ARC and AllCem, whilst lower changes were found in Variolink Veneer, Tetric Flow and Filtek Z350 Flow. The opacity of the materials ranged from −0.01 to 1.16 and its variation was not significant only for Opallis Flow and RelyX ARC.

Conclusions: The accelerated ageing led to colour changes in all the evaluated materials, although they were considered clinically acceptable (ΔE < 3). Amongst the dual-cured resin cements, Variolink II demonstrated the highest colour stability. All the flowable composites showed proper colour stability for the luting of ceramic veneers. After ageing, an increase in opacity was observed for most of the materials.

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1. Introduction

The properties of ceramic veneers, such as colour stability, mechanical strength, compatibility with the periodontal tissues, clinical longevity, enamel-like appearance due to the translucency and superficial texture, makes them an excellent choice for aesthetic treatments.\textsuperscript{1} These materials are excellent for corrections of anatomical malformations with or without tooth preparation, in cases where the patient does not have severe

\textsuperscript{*} Corresponding author. Tel.: +55 41 3271 1637; fax: +55 41 3271 1405.
E-mail address: evesouza@yahoo.com (E.M. Souza).
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doi:10.1016/j.jdent.2011.08.013
discoloration. Currently, there are many commercially available ceramic materials, which can be used to produce laminate veneers with thicknesses ranging from 0.3 to 0.7 mm. Colour changes of the luting agent can become visible, affecting the aesthetic appearance of the final restoration.

The currently available resin cements specifically used for luting ceramic veneers are usually activated by visible light. The main advantages of these cements are their colour stability and longer working time, compared to chemically and dual-cured resin cements. The use of this type of cement makes it easier to remove any excess material before light-curing and reduces the finishing time required after cementation of the restorations. Besides the ease of use, studies have shown that the excellent colour stability of these materials is due to the absence of the amine as a self-curing catalyst, which could cause colour changes in the material over time.

Dual-cured resin cements combine some of the desirable characteristics of light- and chemically cured resin cements. Besides the advantage of allowing further chemical curing in deeper areas where the light is attenuated, dual-cured resin cements have also shown superior mechanical properties, such as flexural strength, elastic modulus, hardness and degree of conversion in comparison to the isolated light activation or exclusively chemical curing. However, dual-cured resin cements also contain aromatic tertiary amine in their formulation, which could compromise the colour stability of the cemented restorations over the long-term.

In order to benefit from the physical properties of light-activated composite resins, as well as an improved cost benefit compared to resin cements, some practitioners have been using flowable resin composites for the cementation of ceramic veneers. These materials developed in 1996, present the same particle size of hybrid composites but with a reduction in the viscosity of the mixture and improved handling properties. However, until recently, its use as a luting agent had only been evaluated by an in vitro study, where its bond strength was compared to dual-cured resin cements. Hence, the optical properties of this material, with respect to its colour stability, have not been yet investigated. The accelerated ageing process has been used to simulate the oral conditions for a relatively long service time. The most commonly used tests for ageing of resin-based materials are prolonged water storage and exposure to ultraviolet light.

With developments in new formulations and polymerization techniques, clinical longevity and colour stability of resin cements are expected to improve. However, changes in the opacity of these materials have been scarcely investigated. On one hand, the role of opacity on the aesthetic performance of ceramic veneers can rely on the ability of the cement to cover underlying tooth discolorations, on the other hand, it may render the restoration less lively. Thus, it becomes relevant to investigate this optical property for adequate selection of luting agent, as well as its long-term evaluation by artificial ageing methods.

The aim of this paper was to evaluate the colour stability and variation in opacity of dual- and light-cured resin cements and flowable composites after accelerated ageing. The null hypotheses tested in this study were: (a) The colour stability and opacity of different luting agents would not be affected by accelerated ageing; (b) the colour stability and opacity of the flowable composites used as cements would be similar to the dual- and light-cured cements; and (c) the colour stability and opacity of the tested materials would remain within a level of clinical acceptance after accelerated ageing.

2. Materials and methods

Three types of materials (dual-cured resin cement, light-cured resin cement and flowable composites) as well as 3 brands of each type from different manufacturers were investigated for the cementation of laminate veneers (Table 1). All the materials were handled in accordance with the manufacturers’ instructions for the cementation of ceramic veneers using shade A3 Vita for standardization purposes.

2.1. Simulation of ceramic veneers

Sixty-three disks were fabricated with ceramic-pressed IPS Empress® Esthetic (Ivoclar Vivadent AG, Schaan, Liechtenstein) in shade ETC 2. The ceramic surfaces were finished and polished using SiC papers from #280 to #2200 in order to assure surface standardization. The discs were 16 mm in diameter and 0.75 mm in thickness. The specimens’ dimensions were confirmed using a digital caliper (Mitutoyo Corp., Tokyo, Japan) at three points on the disc.

2.2. Evaluation of colour stability

To analyse the colour stability, the luting agents were bonded to the previously made ceramic discs. On each disc, the area designated for contact with the cement material was prepared with 10% hydrofluoric acid (FGM Dental Materials, Joinville, SC, Brazil) in gel, applied for 1 min, then rinsed with water for 20 s and dried with oil-free air. Following this, a mono-component silane (ReliX Ceramic Primer – 3M ESPE, St. Paul, MN, USA) was applied to the conditioned surface and left undisturbed for 1 min prior to the application of the catalyst (Adper Scotchbond – 3M ESPE, St. Paul, MN, USA). After the manipulation according to the manufacturer’s specifications, each material was inserted onto a Teflon mould (15 mm × 0.2 mm) which had three triangle-shaped grooves in the periphery to allow the flow of the excess of material. The mould was placed over an acetate sheet placed on a glass plate with a black background to avoid light reflection. The prepared ceramic disc was then placed above the mould and pressed with pliers for 30 s to ensure a uniform cement thickness. The cement was light-cured directly on the ceramic disc using a LED curing unit (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) for 40 s, at four equidistant points of the disc. The light irradiance was measured with a radiometer (LED Demetron, Demetron Research Corp., Danbury, CT, USA) and confirmed for all groups at 850 mW/cm². The specimens of each experimental group (n = 7) were stored in a lightproof container at 37°C under high-humidity condition for 24 h.

After this period, the initial colour measurements (baseline) were determined using a spectrophotometer (Model SP62, X-Rite, Grandville, MI, USA) after calibration using a white standard (calibration plate, \(L^* = 95.17, a^* = -0.96, b^* = 0.46\)). Each specimen was rotated 90 degrees clockwise in the
spectrophotometer and the measurements were performed in triplicate. The colour readings were performed according to the CIE L*a*b*. The specimens were initially placed on a black background, with the ceramic always facing the measurement site, and then on a white background, in order to prevent the potential effects of absorption from any other colour parameters being measured.

Following the initial colour measurements, the specimens were mounted on an acrylic panel and subjected to an accelerated ageing process in a weathering machine (Ci4000 Weather-Ometer, Atlas Electronic Devices, Chicago, IL, USA), according to ASTM G155, Cycle 1. The equipment performed a continuous irradiation of light from a xenon arc bulb with a borosilicate glass filter to 0.35 W/m²/nm at a wavelength of 340 nm. The black panel temperature was 63 ± 2 °C and the cycles were set to 102 min of light plus 50% humidity and 18 min of light plus water spray. The specimens were aged for 120 h at a total energy of 150 kJ.

A new spectrophotometric evaluation was performed under the same initial conditions, following the accelerated ageing process in order to determine both the degree of colour change and opacity of the materials tested. The colour stability was determined by colour differences (ΔE) using the coordinates L*, a* and b* in the baseline (b) and following accelerated ageing (a), as follows:

\[ \Delta L^* = L_a^* - L_b^* \]
\[ \Delta a^* = a_a^* - a_b^* \]
\[ \Delta b^* = b_a^* - b_b^* \]

The colour change (ΔE) was calculated using the following formula:

\[ \Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \]

The opacity parameter (OP) was determined as a percentage of L* values, obtained from the measurements using a black background and a white background, before and after the accelerated ageing and in accordance with the following equation:

\[ \text{OP} = \frac{L^* \text{with black background}}{L^* \text{with a white background}} \times 100 \]

### 2.3. Statistical analysis

One-way ANOVA was performed for both colour change and opacity values. The Tukey HSD test was used for multiple comparisons between groups and Student’s t test was used for the comparisons of opacity before and after accelerated ageing. All tests were performed with a significance level of 5% using the statistical package SPSS 17.0 (SPSS Inc., Chicago, IL, USA).

### 3. Results

#### 3.1. Colour stability

Although all materials were used in A3 shade the initial values of L*, a* and b* suggested slight colour variations amongst the sets of cement/ceramic.

The results of ANOVA showed significant differences amongst the tested materials (p < 0.05). Table 2 presents the
results of colour change for the cementing materials evaluated during this study. Amongst the dual cements, RelyX ARC and AllCem showed the greatest changes in colour, whilst Variolink II was similar to the Opallis Flow composite. Amongst the light-activated cements, RelyX Veneer and Experimental Veneer showed no significant differences in colour changes between each other, although they exhibited greater colour changes than Variolink Veneer. The latter represented the lowest ΔE means, together with Filtek Z350 Flow and Tetric Flow composites (p > 0.05).

Based on the analysis of changes in value or lightness (L’), most of the evaluated materials darkened, with the highest ΔL’ attributed to the dual cement AllCem. Changes in the reddish-green hue (a’) were very small for all materials. Whilst changes in bluish-yellow hue (b’) ranged between positive and negative values, with greater tendency towards the blue on cement RelyX ARC and a greater tendency towards yellow on cement AllCem.

3.2. Opacity

Table 3 shows the mean variation in opacity of the materials evaluated, before and after accelerated ageing. There were found statistically significant differences amongst the materials before ageing, after ageing and variation in opacity (p < 0.05). RelyX Veneer presented significantly higher values of opacity before and after accelerated ageing (p < 0.05). Lower values of opacity were found in Experimental Veneer, Variolink Veneer and Tetric Flow, in both conditions.

The opacity of all materials increased after accelerated ageing, with the exception of Opallis Flow. However, the variation of opacity was not significant for Opallis Flow and RelyX ARC (p > 0.05).

4. Discussion

This study evaluated the colour stability of materials for luting of ceramic veneers using a set of cement/ceramic for the analysis. Many studies17,18,20,21 regarding the colour stability of resin cements used specimens built entirely with the luting agent in thicknesses that are not clinically compatible with the film below laminate veneers.27 In the present study, the luting agents were 0.2 mm thick bonded to a 0.75 mm ceramic disc in order to reproduce clinical condition and to avoid overestimated results regarding the effect of colour changes of the underlying material. Other previous studies assessed of colour stability of resin cements below ceramic veneers showed less colour changes than that of cement itself.7,23,28 The literature also suggests that ceramic restorations have varied opacities and for this reason the colour change of the cementing agent could be masked.20 The ceramic used in the current study has translucent characteristics, besides being used in very low thickness in order to provide evidence of any significant colour changes of the luting material. It was shown in a previous study7 that 0.5 mm thick porcelain disc would not mask the difference in hue amongst different luting materials.

The accelerated ageing carried out in the present study using a weathering chamber model submitted the samples to increased temperature, humidity and ultraviolet light. These conditions can induce an oxidation process of the amine,
component used as initiator of resin cements. Hekimoglu et al. conducted accelerated ageing in a weathering machine, with times ranging from 300 h to 900 h and did not observe any differences in colour changes during the longest periods. The present study used similar equipment but with a temperature of 63 °C, which could further accelerate the ageing of the tested materials. The results from the current study provide a comprehensive assessment of the colour stability of materials that may be used for luting ceramic veneers. The literature is scarce regarding the new-developed light-cured resin cements that are available exclusively for the luting of ceramic veneers, and also there are currently no specific comparisons between them. Previous investigations evaluated only the base paste (light-activated) of dual resin cements compared to the mixture of both pastes (dual mode) whether or not they were submitted to light curing. However, this is not the primary indication, since usually the best properties are achieved with the mixture of both pastes of dual resin cements.

Different instruments have been developed to reduce or overcome imperfections and inconsistencies of traditional shade matching using shade guides. Spectrophotometers are today amongst the most accurate, useful and flexible instruments for colour matching in Dentistry. The data obtained from spectrophotometers are manipulated and translated into a form useful for dental professionals. The advantages of spectrophotometric analysis with the CIE L*a*b* system are the detection of colour changes that are not visible to the human eye and the ability to express colour differences in units that may be related to visual perception and clinical significance. There is some controversy in literature regarding the values of clinically noticeable colour changes. Vichi et al. used three different ranges for distinguishing colour differences: ΔE values lower than 1.0 were considered undetectable by the human eye, values between 1.0 and 3.3 were considered visible by skilled operators, but clinically acceptable, and ΔE values greater than 3.3 were considerable appreciable also by non-skilled persons and for that reason clinically not acceptable. Chang et al. reported the gold standard threshold of 2.0, which was considered a perceptible colour change able to determine the optical effect of resin cements. In a recent study, a ΔE = 1.6 represented the colour difference that could not be detected by the human eye. However, most studies report ΔE ≤ 3.3 as clinically acceptable. The colour changes in the present study ranged from 0.41 to 2.40, regardless of the type of material, which would be within the previously mentioned conditions. These findings corroborate with those from Noie et al., where significant differences were found between dual and light-activated cements, although they were not visually perceptible.

All the flowable composites and light-activated resin cements showed values of ΔE less than 1.0, possibly because all of them have only a physical curing reaction. The oxidation of the aromatic amine, required for the initiation of the polymerization reaction of composite resins might be the main reason for changes in the colour of dual resin cements. As the light-activated materials have only aliphatic amines in their composition, the trend is for less colour change to occur than with the dual cements, which have both aliphatic and aromatic amines. In the present study, the dual-curing resin cements showed colour changes higher than 2.0, except for Variolink II, which showed ΔE less than 1.0, similar to that of light-activated materials. This result may be due to a higher concentration of photosensitive components compared to the chemical cured components in this material. Nathanson and Banas reported less colour change of Variolink II with a light-curing mode (only the base paste) in comparison to a dual mode. Other studies found no differences in ΔE between the dual- and chemical modes of Variolink II. The chemical activation of this resin cement resulted in lower flexural strength, modulus and hardness compared to the light and dual curing modes. These results demonstrate the importance of the light activation and the possible largest amount of photosensitive components present in this cement.

The negative values of ΔL* for all materials, except for RelyX ARC, are consistent with the literature and suggest that resin-based materials tend to darken after accelerated ageing. The smallest variations were found in a* coordinates and the greatest in the b* coordinates, with the highest negative value attributed to RelyX ARC (–2.38), indicating a tendency towards blue and the highest positive value for AllCem, suggesting yellowing of this cement. According to some authors, the yellowing of a material over time could be related to an increased amount of camphorquinone in its formulation. Another explanation for the tendency of yellowing could be the exposition of Bis-GMA-based material to ultraviolet light and heat. The smallest colour changes in the b* axis were assigned to the products from Ivoclar (Variolink II, Variolink Veneer and Tetric Flow), which may be related to a lower amount of Bis-GMA or a lack of it in the formulation of the material, as in the case of Variolink Veneer (manufacturer’s information).

Colour changes in the materials are related to the changes in the resin matrix and in the silanization process of the filler particles, causing higher water sorption. The presence of UDMA can contribute to a reduction in the amount of TEGDMA, which is the monomer responsible for higher rates of water sorption in resin-based materials due to its hydrophilic ether linkages. Therefore, materials that replace part of TEGDMA for UDMA may have less colour change. A previous study showed that the size and number of particles can also influence the values of ΔE, ΔL*, Δa* and Δb*, as well as the translucency of composite resins.

In this study, although all the materials match the colour A3, it was found that initial opacity ranged from 47.44 to 61.14. The material RelyX Veneer presented the highest values of opacity, which was to be expected since the manufacturer classifies this material as opaque. The opacity of all materials increased after ageing, with the exception of composite Opallis Flow, which is in accordance with a recent study. The variation of opacity was significant for most of the materials evaluated. Although there is no literature suggesting the level of clinical acceptability in variations of opacity, the values obtained in this study are reduced and probably imperceptible to the naked eye. Joiner pointed out the importance of optical properties such as translucency and opacity, since they are indicative of the quality and quantity of the reflected light.

Since the specimens size used for the spectrophotometric analysis in the current study were 16 mm, it was not possible
to use a dental substrate in order to assess more accurately the possible changes of veneer/cement/tooth assemblies.

The first hypothesis proposed for this study was rejected, since the materials changed in colour and opacity after the accelerated ageing process. The additional hypotheses were accepted, since flowable composites showed similar colour change to that of resin cements. Also, light- and dual-cured cements and flowable composites showed acceptable colour stability ($\Delta E < 3$) and opacity for ceramic veneer luting. These findings suggest that clinicians can use dual-cured resin cements in aesthetic clinical cases. However, for those unwilling to take risks in front of an observer with more accurate visual perception, the use of light-cured cements and flowable composites could be considered more suitable due to their higher colour stability.

5. Conclusions

- The accelerated ageing led to colour changes in all the evaluated materials, although they were considered clinically acceptable ($\Delta E < 3$);
- After the ageing process, an increase in opacity was observed for most of the materials;
- Variolink Veneer, Filtek Z350 Flow and Tetric Flow showed higher colour stability than the other tested materials;
- Amongst the dual-cured resin cements, Variolink II demonstrated the highest colour stability ($\Delta E < 1$);
- All the flowable composites showed proper colour stability for the luting of ceramic veneers.

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