Effect of aging on color stability and bond strength of dual-cured resin cement with amine or amine-free self-initiators

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INTRODUCTION

The resin-based luting agents are widely used for luting porcelain restorations to teeth due to their natural appearance, high bond strengths, low solubility, and superior mechanical properties11. Bond strengths and color stability are related to the long-term success of restorations. The polymerization modes of resin cements could be classified into light-polymerization, chemical-polymerization, and dual-polymerization. Light-cured (LC) resin cements are particularly recommended in thin and transparent porcelain restoration bonding because of their manageable working time and long-term color stability14. Whereas light-cured resin-based luting agents are based on light curing and more suitable for porcelain laminate veneers (PLVs) than dual-cured (DC) resin-based ones9. However, their mechanical properties, for instance, flexural strength, degree of conversion, rigidity, and elastic modulus, are usually inferior to the dual-cured ones10,11. The insufficient cure could reduce the resin cement’s mechanical capacity and even lead to the debonding of restoration in the long-term. Dual-cured resin cements have been widely used for their excellent performance in deep cavities or opaque areas. They could chemically cure at deepened or opaque areas where light intensity is hard to reach9,11. However, Koishi et al. reported that the oxidation of residual aromatic tertiary amines in the dual-cured resin cements might give rise to color alteration over time12. Besides, the polymeric matrix’s degradation, unreacted monomers, filler size, and extrinsic environment may affect the color stability in luting agents1,13,14.

Several ingredients could be added to modify the dual-cured resin cements to obtain long-term color stability. Smith et al.15 introduced a novel dual-cured resin cement without benzoyl peroxide/amine redox (chemical accelerator and initiator systems), which owed more color stability than conventional dual-cured resin cement after 12-month storage. Another in vitro study16 gave the same conclusion that resin cements without tertiary amines/benzoyl peroxide possessed less discoloration after 4-week storage. Besides, a randomized clinical trial found no statistical differences in the discoloration between light-cured and dual-cured resin cements after two years of operation17. These results suggested that the dual-cured resin cements containing amine-free self-initiators could be used to bond all-ceramic restorations with long-term color stability. However, whether the color and bond strengths of such resin cements could fulfill the clinical requirements in the long-term durability has not been investigated.

This study aimed to evaluate the color stability and the micro-shear bond strengths (μSBS) of dual-cured resin cements containing amine or amine-free self-initiators. Three dual-cured and one light-cured resin cements were used. The covered (by lithium disilicate ceramic disks) and uncovered groups (n=10) were included. Color measurements were tested after 24 h, 10,000 and 20,000 thermal cycles (TCs). Micro-shear bond strengths (μSBS) were tested after 24 h, 10,000 and 20,000 TCs, and failure modes were analyzed (n=14). Two-way ANOVA and Tukey’s test were implemented for color difference (ΔE*ab) and μSBS (α=0.05). The mean ΔE*ab difference was significant among groups (p<0.001). The lowest ΔE*ab values were obtained for dual-cured resin cement with amine-free self-initiators dual-cured cement after aging in all dual-cured resin cements, and the μSBS of the dual-cured resin cements on ceramic was significantly higher than that of the light-cured ones after aging (p<0.001).

Keywords: Resin cement, Initiators, Color stability, Bonding, Accelerated aging

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MATERIALS AND METHODS

Materials
The primary materials used in this study are listed in Table 1. Power analysis was conducted using G-power software (version 3.1; Heinrich-Heine-Universität, Düsseldorf, Germany) to determine the sample size. Three dual-cured resin cements with their corresponding ceramic primers were used as the experimental groups for the μSBS test: PANAVIA V5/Clearfil Ceramic Primer Plus (V5/CCP; Kuraray Noritake Dental, Tokyo, Japan), PANAVIA F2.0/ Clearfil Ceramic Primer Plus (F2.0/ CCP; Kuraray Noritake Dental), and Rely X Unicem 200/Scotchbond Universal (Un/SBU; 3M ESPE, St. Paul, MN, USA). One light-cured resin cement with its corresponding ceramic primer was used as the control group: Variolink Esthetic/Monobond N (Es/MN; Ivoclar Vivadent, Schaan, Liechtenstein). However, these primers seemed different in translucency and color when applying to the ceramic surface, especially universal primer (Scotchbond Universal 3M ESPE) is a translucent yellow liquid. Therefore, we chose the other ceramic primer (Porcelain Etch and Silane, Ultradent, South Jordan, UT, USA) which was transparent and monofunctional to avoid the possible influence on the color stability measurements. Lithium disilicate ceramic (IPS e.max Press HT A1, Ivoclar Vivadent) was used to fabricate the thin ceramic disk and mimic veneer restoration in the clinical situation.

Sample preparation
Forty lithium disilicate ceramic disks (0.5 mm in thickness and 10 mm in diameter, HT, A1, IPS e.max Press, Ivoclar Vivadent) were sintered via lost-wax and hot-press technologies to simulate veneers in vitro for color measurements. Both surfaces were polished with 600-, 800-, and 1200-grit SiC sandpapers under running water for each disk. These disks were examined using a digital micrometer (Shanghai Taihai Measuring Tools, Shanghai, China) to ensure a 0.5±0.05 mm thickness for further color measurements. The other 168 lithium disilicate ceramic blocks (8×6×2 mm, IPS e.max Press, Ivoclar Vivadent) were fabricated and polished in the same method preparing for the μSBS test.

Color stability measurement
All the lithium disilicate ceramic disks were randomly divided into four groups (n=10). All these ceramic disks were etched with 9% hydrofluoric (HF) acid (Porcelain Etch and Silane, Ultradent) for 90 s. They were washed in distilled water for 15 s, and dried with oil-free air after etching. The silane primer (Porcelain Etch and Silane, Ultradent) was applied to the disks’ treated surfaces and air-dried for the 60 s. The etched and silanized disk was placed at the bottom of a Teflon ring mold with 10 mm inner diameter and 1 mm thickness (Fig. 1). According to the manufacturer’s specifications, these luting agents were mixed using a plastic spatula (DC) or injected (LC) above the disk. The mold was covered with a glass slide, and 1 kg weight was applied for 10 s to ensure the excess resin cement was extruded. The sample was irradiated closely for 40 s with an LED curing unit (Bluephase Style, 1,100 mW/cm², Ivoclar Vivadent). Then, the ring mold and residual resin around the sample’s edge were carefully removed. Finally, the cured resin cement surfaces were polished with 600-, 800-, and 1200-grit SiC sandpaper under running water to acquire 1.0±0.05 mm samples, and these specimens were defined as the covered groups. Meanwhile, the cement sample disks were fabricated using Teflon ring molds with 10 mm inner diameter and 0.5 mm thickness without ceramic slices, and these specimens were defined as the uncovered groups (n=10). The covered groups simulated the PLV in clinical practice, whereas the uncovered groups mimicked the luting agents exposed to the oral cavity. Three dents were severally cut at the edge of the sample surface at each 90° to ensure that color measurement could be performed in the same position. A light dentin color cylinder was fabricated (ND2 color, 10.0 mm in diameter, 4.0 mm thick, Natural Die Material, Ivoclar Vivadent) for the background to simulate dentin substrate. These specimens were stored at 37°C distilled water for 24 h in the dark. The complexes (sample-background) were fixed on a customized jig, with the gap between them full of distilled water. The 2° observer configuration and standardized illumination source D65 (OL 53, Optronic Laboratories, Orlando, FL, USA) were employed. Baseline color recordings were tested using a spectrophotometer (PR-655 SpectraScan, Photo Research, Chatsworth, CA, USA) outfitted with MS-75 and SL-0.5× lens. Then, the Commission International de l’Eclairage (CIE) L*a*b* values were determined. The spectrophotometer was adjusted to a white calibration standard plate offered by the manufacturer before the color evaluation. The L*a*b* color values were continuously measured three times, and the mean was calculated as the baseline data of the specimens. Afterward, all specimens were thermal cycled between two water baths (Thermo Scientific, Waltham, MA, USA) at 5°C and 55°C for 30 s for each dwell time. After 10,000 and 20,000 thermal cycles (TCs), color measurements were reconduted separately. The CIE color difference (ΔE*ab) between the baseline and after two TCs times was figured up using a formula: ΔE*ab=[(ΔL*)²+(Δa*)²+(Δb*)²]½, where L* stands for lightness, from 0 (black) to 100 (white), a* corresponds to green (negative) to red (positive) and b* to blue (negative) to yellow (positive), both ranging from −128 to +127. ΔE*ab=2.7 refers to 50%-50% acceptability. Thus, the ΔE*ab value above 50%-50% was unacceptable.

μSBS test
A total of 168 prepared ceramic blocks (8 mm in length, 6 mm in width, and 2 mm in thickness) were randomly divided into four groups (n=42). All the ceramic blocks were etched with 9% HF acid for 90 s, rinsed with distilled water for 15 s, and dried with oil-free air. Each group was then treated with silane following the manufacturer-recommended protocols: V5/CCP, F2.0/ CCP, Un/SBU, and Es/MN. Translucent Teflon tubes (1
| Product and code | Shade | Polymerization and initiator system type | Content | Manufacturer | Application procedure |
|-----------------|-------|------------------------------------------|---------|--------------|-----------------------|
| **Resin cement** |       |                                          |         |              |                       |
| PANAVIA F2.0 (F2.0) | Light | Dual cure (benzoyl peroxide, amine, dl-camphorquinone for initiator) | Paste-A: 10-MDP, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, silanated silica filler, silanated colloidal silica, dl-camphorquinone, catalysts, initiators Paste-B: Hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, silanated barium glass filler, surface treated sodium fluoride, catalysts, accelerators, pigments | Kuraray Noritake Dental, Tokyo, Japan | The paste mixed applied using a plastic spatula was placed, and light-cured for 40 s. |
| PANAVIA V5 (V5) | Clear | Dual cure (Highly stable peroxide, a non-amine reducing agent, Di-Camphorquinone for initiator) | Paste A: Bis-GMA, TEGDMA, Hydrophobic aromatic dimethacrylate, Hydrophilic aliphatic dimethacrylate, Initiators, new chemical polymerization accelerators, Silanated barium glass filler, Silanated, fluoroaluminosilicate glass filler, Colloidal silica Paste B: Bis-GMA, Hydrophobic aromatic dimethacrylate, Hydrophilic aliphatic dimethacrylate, Silanated barium glass filler, Silanated aluminum oxide filler, new chemical polymerization accelerators, Di-Camphorquinone, Pigments | Kuraray Noritake Dental | The paste mixed applied using a plastic spatula was placed, and light-cured for 40 s. |
| Rely X Unicem 200 (Un) | Translucent | Dual cure self-adhesive (Sodium p-toluenesulfinate, amine, camphorquinone for initiator) | Base paste: TEGDMA, methacrylate monomers containing phosphoric acid groups, methacrylate monomers, silanated fillers, initiator components, stabilizers, rheological additives Catalyst paste: methacrylate monomers, alkaline fillers, silanated fillers, initiator components, stabilizers, pigments, rheological additives | 3M ESPE, St Paul, MN, USA | The paste mixed applied using a plastic spatula was placed, and light-cured for 40 s. |
| Variolink Esthetic LC (Es) | Neutral | Light cure (Ivocerin for initiator) | UDMA and further methacrylate monomers, ytterbium trifluoride, and spheroid mixed oxide, Ivocerin, stabilizers, and pigments | Ivoclar Vivadent, Schaan, Liechtenstein | The paste from syringe was placed, and light-cured for 20 s. |

**Ceramic primer**

| Clearfil Ceramic Primer Plus (CCP) |       | 3-Methacryloxypropyl trimethoxysilane, MDP, Ethanol | Kuraray Noritake Dental | Apply on the ceramic for 15 s and air-dry gently. |
| Scotchbond Universal (CBU) |       | MDP phosphate monomer, dimethacrylate resins, HEMA, Vitrebond copolymer, filler, ethanol, water, initiators, silane | 3M ESPE | Applied and rubbed on the surface for 20 s and gently air-thinned for about 5 s until it does not move. |
| Monobond N (MN) |       | Alcohol, silane methacrylate, phosphoric acid Methacrylate, sulphide methacrylate | Ivoclar Vivadent | Apply on the ceramic for 60 s and air-dry gently. |
| Lithium disilicate ceramic material |       | SiO₂: 57–80%, Li₂O: 11–19%, K₂O: 0–13%, P₂O₅: 0–11%, ZrO₂: 0–8%, ZnO: 0–8%, others: 0–10% | Ivoclar Vivadent | — |
Fig. 1 The schematic diagram of sample preparation and color stability measurement. A: The pre-prepared ceramic disk was placed at the bottom of a Teflon ring mold, and resin cement was injected above the disk for sample preparation (the covered group). The cement sample disks were fabricated using the Teflon ring mold for sample preparation (the uncovered group). B: the prepared sample: the covered group and the uncovered group. C: The complexes (sample-background) fixed on a customized jig were tested using a spectrophotometer under a standardized illumination source D65 condition. C: ceramic; R: resin cement; SIS: standardized illumination source D65; S: spectrophotometer.

Fig. 2 Schematic of µSBS specimen preparation and µSBS test. µSBS: micro-shear bond strength, RC: resin cement, Jig: fixture to hold specimens, SF: stainless filament, UTM: universal testing machine, C: ceramic.

According to the proportion of residual resin on the adhesive surface(21-23), the failure modes were categorized as adhesive failure (<1/3), cohesive failure (≥2/3), and mix failure (>1/3 but <2/3).

RESULTS

Color stability measurement
The mean and standard deviation of the ΔE*ab, ΔL*, Δa*, and Δb* values for each period were shown in Tables 2 (uncovered groups) and 3 (covered groups). The results showed significant color changes among the tested materials in ΔE*ab values (p<0.05). The mean ΔE*ab values of all groups were 0.88–3.71. The mean ΔE*ab values of the covered groups were 0.88–3.02, while those of the uncovered groups were 1.61–3.71. The ΔE*ab values of Es groups were all lower than 2.7 in the uncovered or covered groups.
The $\Delta E_{ab}$ differed with that of the control group (Es) under the 10,000 and 20,000 TCs were above 2.7 and statistically different after 20,000 TCs ($p>0.05$). The values with the same uppercase letters are not statistically different after 10,000 TCs ($p>0.05$). The values with the same lowercase letters are not statistically different after 20,000 TCs ($p>0.05$).

In the uncovered groups (Table 2), the mean $\Delta E_{ab}$ value of F2.0 was all above 2.7. The $\Delta E_{ab}$ of F2.0 at 10,000 and 20,000 TCs were above 2.7 and statistically differed with that of the control group (Es) under the same storage ($p<0.05$). The $\Delta E_{ab}$ of the Un at 10,000 TCs were below 2.7, and their difference with those of Es was not statistically significant ($p=0.998$). However, after 20,000 TCs, the difference between the $\Delta E_{ab}$ of the Un and Es was statistically significant ($p<0.05$). The V5 group displayed the lowest $\Delta E_{ab}$ values among all the dual-cured resin cement groups under the same aging level (10k TCs or 20k TCs), and no statistical significance was found in the difference between the V5 group and the Es group (10k TCs: $p=0.559$; 20k TCs: $p=0.994$).

In the covered groups (Table 3), The $\Delta E_{ab}$ of the Un groups had the highest values among all luting agents after 10k TCs or 20k TCs. The $\Delta E_{ab}$ over 2.7 was found in only the Un group after 10,000 TCs. However, after 20,000 TCs, this $\Delta E_{ab}$ was below the threshold. No statistical significance was found between the $\Delta E_{ab}$ of Un after 10,000 and 20,000 TCs ($p=0.113$). The V5 groups presented the least discoloration in all the resin cement groups after 10k or 20k TCs as well (10k TCs: $\Delta E_{ab} = 0.88 \pm 0.51$; 20k TCs: $\Delta E_{ab} = 0.96 \pm 0.60$).

**µSBS test**

The mean and standard deviation of the µSBS values for each group are shown in Table 4. The two-way ANOVA for the µSBS test revealed that “resin cements” and “storage conditions” influenced the µSBS significantly ($p<0.001$), and the interaction between the two factors was significant ($p<0.001$). After 24-h in distilled water, the µSBS of Un showed the highest bond strengths in all groups, whose statistical difference was significant.

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### Table 2 Mean (standard deviation) CIE Lab values for four resin cements after different thermal cycling times resin cement in the uncovered groups

| Resin cement | Thermal cycles | $\Delta E_{ab}$ (SD) | $\Delta L^*$ (SD) | $\Delta a^*$ (SD) | $\Delta b^*$ (SD) |
|--------------|---------------|---------------------|------------------|------------------|------------------|
| F2.0         | 10,000        | 3.04 (0.70)$^b$     | 0.31 (1.30)      | 0.70 (0.24)      | 2.71 (0.49)      |
|              | 20,000        | 3.71 (0.71)$^{ab}$  | 0.36 (1.20)      | 0.91 (0.23)      | 3.40 (0.66)      |
| V5           | 10,000        | 1.61 (0.91)$^c$     | -0.95 (1.01)     | 0.45 (0.15)      | 0.98 (0.61)      |
|              | 20,000        | 2.00 (0.67)$^b$     | 0.69 (1.23)      | 0.49 (0.18)      | 1.29 (0.82)      |
| Un           | 10,000        | 1.94 (0.57)$^c$     | 0.43 (1.03)      | 0.30 (0.21)      | 1.54 (0.69)      |
|              | 20,000        | 3.08 (0.88)$^{ab}$  | 0.47 (0.77)      | 0.44 (0.29)      | 2.85 (1.07)      |
| Es           | 10,000        | 2.09 (0.38)$^c$     | -1.76 (0.47)     | -0.34 (0.11)     | -1.00 (0.21)     |
|              | 20,000        | 1.82 (0.53)$^b$     | -1.75 (0.58)     | -0.15 (0.08)     | -0.34 (0.26)     |

**Table 3**

Mean (standard deviation) CIE Lab values for four resin cements after different thermal cycling times resin cement in the covered groups

| Resin cement | Thermal cycles | $\Delta E_{ab}$ (SD) | $\Delta L^*$ (SD) | $\Delta a^*$ (SD) | $\Delta b^*$ (SD) |
|--------------|---------------|---------------------|------------------|------------------|------------------|
| F2.0         | 10,000        | 1.95 (0.89)$^b$     | -1.85 (0.88)     | 0.23 (0.18)      | 0.06 (0.65)      |
|              | 20,000        | 1.78 (0.69)$^{ab}$  | -0.94 (1.05)     | 0.35 (0.29)      | 0.95 (0.86)      |
| V5           | 10,000        | 0.88 (0.51)$^c$     | -0.47 (0.64)     | 0.23 (0.19)      | 0.48 (0.35)      |
|              | 20,000        | 0.96 (0.60)$^a$     | -0.26 (0.75)     | 0.29 (0.21)      | 0.50 (0.61)      |
| Un           | 10,000        | 3.02 (1.04)$^c$     | -2.88 (0.99)     | 0.00 (0.42)      | -0.11 (0.93)     |
|              | 20,000        | 2.50 (0.92)$^b$     | -2.06 (0.77)     | 0.24 (0.34)      | 0.78 (1.29)      |
| Es           | 10,000        | 2.15 (0.39)$^c$     | -1.41 (0.67)     | -0.50 (0.12)     | -1.44 (0.18)     |
|              | 20,000        | 2.15 (0.40)$^b$     | -1.46 (0.41)     | -0.50 (0.11)     | -1.46 (0.28)     |
Table 4  Mean (standard deviation) micro-shear bond strengths (µSBS) values

| µ-SBS values | F2.0  | V5    | Un    | Es    |
|--------------|-------|-------|-------|-------|
| 24 h WS      | 19.04 (3.33)\textsuperscript{Aa} | 18.00 (3.72)\textsuperscript{Aa} | 20.67 (2.90)\textsuperscript{Aa} | 12.61 (2.06)\textsuperscript{Ab} |
| 10,000 TCs   | 17.18 (1.80)\textsuperscript{Aa} | 13.40 (2.58)\textsuperscript{Bb} | 14.05 (2.73)\textsuperscript{Bb} | 4.85 (2.0)\textsuperscript{Bc} |
| 20,000 TCs   | 13.71 (2.16)\textsuperscript{Ba} | 8.25 (2.25)\textsuperscript{Cb} | 7.37 (2.66)\textsuperscript{Cb} | 2.72 (1.71)\textsuperscript{Bc} |

Mean and standard deviation of µSBS for each group.
Within the same row, the same lowercase letter values were not statistically different ($p>0.05$).
Within the same column, the same large case letters were not statistically different ($p>0.05$).
WS: water storage; TCs: thermal cycles

Fig. 3  Representative scanning electron microscope images of specimens (original magnification×150).
A: Typical cohesive failure, B: Typical mixed failure, C: Typical adhesive failure, Rc: resin cements, Cc: ceramic.

Fig. 4  Failure mode distribution after 24 h, 10,000 and 20,000 thermal cycles.

Failure mode analysis
Images of the adhesion areas’ typical surface morphology under SEM observation were shown in Fig. 3. The distributions and proportions of the areas to the failure modes are depicted in Fig. 4. After 24 h, cohesive failure and mixed failure were the predominant failure modes presented in all groups except the Es groups, and the highest percentage of both failures was 92.86% in the F2.0 group. After 10,000 TCs, the proportion of cohesive failure and mixed failures declined. However, in the F2.0 groups, the proportion of adhesive failure remained at 7.14%. After 20,000 TCs, the proportion of cohesive failure and mixed failures of F2.0 declined to 35.71%. Adhesive failure was the only failure pattern in the Es groups before and after thermocycling.

DISCUSSION
The results showed that the color variation among the resin cements with amine or amine-free self-initiators was significant. The resin cement containing new self-initiator systems rather than conventional tertiary amines/benzoyl peroxide displayed better stability than the traditional resin cements containing amine self-initiator systems. Therefore, the first null hypothesis (dual-cured resin cements containing amine or amine-free self-initiators do not lead to significant color variation in accelerated aging) was rejected. This phenomenon was consistent with Alkurt and Duymus, who found that resin cement with amine-free self-initiator systems (V5) has enhanced color stability\textsuperscript{24}. The current study attempted to simulate intraoral
condition, using a light dentin color background simulated an abutment tooth and ceramic disks bonded by resin cements to simulate the clinical situation. Storage with distilled water and thermal cycling were chosen for artificial modeling, and 10,000 TCs of accelerated aging in vitro corresponded to 1 service year in human’s oral condition. High transparency ceramic was chosen because the more irradiance passed through it, and the higher color variation resin cement may present beneath the ceramic, the higher $\Delta E^{*ab}$ value of the ceramic–cement complex was measured. The porcelain slices possess high transmittance and shallow thickness to prove distinct color variation in the resin cement. Some previous studies considered the $\Delta E^{*ab}$ values of 2.2–4.4 as clinically acceptable. Recent studies observed upper central incisors or monochromatic ceramics in a group of volunteers, including professional dental staffs and laypersons, to determine the 50%:50% acceptability threshold: the $\Delta E^{*ab}$ values are above 2.7. Thus, the $\Delta E^{*ab}$ value of 2.7 was chosen as the acceptability threshold in the present study.

Some manufacturers have recently developed a new dual-cured resin cement with amine-free initiator systems, and it had more color stability than the conventional dual-cured one. Chemical-cured catalytic systems in dual-cured resin cements are more prone to color changes than the light-cured catalytic systems in light-cured ones because the reactant of benzoyl peroxide and aromatic tertiary amines are susceptible to degradation. In contrast, aliphatic amines in light-cured cements are less sensitive to the curing process. Studies reported that none of the light-cured or dual-cured groups display statistical significance in $\Delta E^{*ab}$ before and after accelerated aging ($p>0.05$), and all the $\Delta E^{*ab}$ values are below the acceptability threshold. A randomized clinical trial in vivo assessed the discoloration and marginal discoloration of light- and dual-polymerizing cements luting on PLVs; the outcome was similar to that of the previous study, that is, the $\Delta E^{*ab}$ of the dual-polymerization cement ($\Delta E^{*ab}=1.57$) was lower than that of the light-polymerization cement ($\Delta E^{*ab}=2.31$) under 24-month evaluation. These studies used the same commercial cement model (Variolink II) but different curing modes (light or dual polymerization). These phenomena may be explained by the base containing aliphatic and aromatic tertiary amines being light-cured only. However, the aromatic amines do not mix with benzoyl peroxide in the catalyst, thus remaining intact.

In the uncovered groups, the dual-cured cement V5 group had the lowest $\Delta E^{*ab}$ values than the other dual-cured groups (F2.0 and Un) and did not show any statistical difference comparing to the control groups. Oei et al. reported the commercial dual-polymerizing luting agent containing a new chemical-cured initiator system (allyl thiourea/cumene hydroperoxide) added has low-color property and lessened drastic color variation after accelerated aging conditions. For conventional dual-polymerizing resin-based luting agents, the color change in intrinsic factors is related to the hydrolysis of organic constituents in resin-based materials, mainly the filler type and content, resin matrix component, the curing type and the residual unreacted monomer. Besides, the tertiary amines used as chemical co-initiators in dual-resin-based materials affect color stability. Dual-cured resin cements are prone to be discolored because of the degradation of aromatic tertiary amines, while the aliphatic amines in light-cured cements tend to be stable. The residue of unreacted benzoyl peroxide could give rise to color variation as well. In the present study, the result implied that the chemical catalytic system of V5 was made up of highly stable peroxide and non-amine reducing agent, which had less discoloration than conventional benzoyl peroxide/amine redox accelerators and initiator systems.

In the covered groups, the V5 group still presented the least discoloration among all dual-cured resin cements, which was consistent with the reference as mentioned above. Furthermore, literatures indicated that polymerized resin cements beneath dental ceramics had less discoloration than the same type of monolithic resin cement specimens. In these studies, the ceramic slices were thicker than those in the current study (0.7–1.0 mm). After 20,000 TCs in the uncovered groups, the dual-cured cements $\Delta E^{*ab}$ (Un and F2.0) exceeded the acceptability threshold, with statistical differences with that in the Es. In the covered groups, After 20,000 TCs in the covered groups, the $\Delta E^{*ab}$ value of the Un group below the acceptability threshold and does not significantly differ from that of the Es group. However, the $\Delta E^{*ab}$ value of the Es in the covered groups was similar to that in the uncovered groups, indicating that Es has relative color stability. These phenomena implied that beneath the highly transparent and thin lithium disilicate ceramics, the discoloration in conventional resin cement containing amine self-initiator could be easily measured. V5 exhibited color stability whether or not the sheathed porcelain slice cement on it. Similar to Kilinc’s study, the uncovered resin slices were more exposed to hot and ice stimulation and not entirely imitated beneath the ceramic restoration, which may lead to more color stability declined than the covered groups.

In the long-term, resin cement discoloration could be due to extrinsic and intrinsic factors. The extrinsic factors of resin cements include food, smoking, and beverages. And most of the intrinsic factors were attributed to the structure of the resin cements themselves: polymerization type, compositions of resin matrix and filler, and the presence of unreacted monomer. Ferracane et al. found that the smaller the filler particles, the smaller the amount of water absorbed by the composites matrix, which leads to lower aging susceptibility, and consequently, lower color change. The filler particles size of V5 (0.01–12 µm) and Es (0.04-0.2 µm) were smaller than Un (12.5 µm) and F2.0 (0.04–19 µm), which might be one reason why the color stability of V5 and Es better than Un and F2.0. But Schneider et al. concluded that a matrix with lower water solubility was related to hardness but not necessarily to
color stability, which was opposite to the former one\(^{37}\). According to Turgut and Bagis, composites have large filler particles and a relative rough surface, so they are more susceptible to staining\(^{4}\). Other investigators have concluded that lighter shades of composite resins tend to higher color degeneration after a short period of water storage\(^{38,39}\). Our study chose the same or approximate color cements to avoid the former phenomenon as much as possible.

The \(L^*\) values all decreased in the covered groups, but except PANAVIA V5 in 10,000 thermal cycles and Variolink Esthetic in the uncovered groups, other groups \(L^*\) values were all slightly increased. Many studies reported that aging reduced the \(L^*\) values laminate veneer-luting agent complex\(^{18,40,41}\). The reductions of \(L^*\) values could be related to increased pigment content in the materials’ bulk. These specimens in the studies as mentioned above were immersed in distilled water and not external pigments, which suggested that the darkening phenomenon was due to the remains of oxidized or unreacted components in the polymer. The ingredients might serve as intrinsic staining agents.

On the contrary, Ramos et al. only studied monolithic resin cement specimens and found both the increasing and decreasing in \(L^*\) values\(^{42}\). Albuquerque et al. study showed that 24 h to 1-month water storage after polymerization, all monolithic composite resins showed a slight increase in \(L^*\) values\(^{31}\). The polymerization between the resin monomers continued after the initial light activation, which led to brightness. If oxidized and unreacted components of the polymerization system were eluted, intrinsic staining agents of the system were reduced, the less intense color variation could be expected\(^{42,43}\). Kilinc et al. evaluated both monolithic luting agents’ color stability and laminate veneer-luting agent complex after artificial aging. The results showed increased and decreased \(L^*\) values whether resin cements in veneered or uncovered groups\(^{40}\). Another randomized clinical trial concerning the color alteration of veneers cemented to enamel resin cement observed that \(L^*\) values were decreased at 2 months and 6 months, but turning to be increased at 12 months and 24 months\(^{19}\). In conclusion, the decrease or the increase of \(L^*\) values may be treated as a multi-factor superimposed effect. The color difference evaluation might give us the information about the color stability of laminate veneer-luting agent complex and monolithic luting agents themselves.

The positive \(\Delta b^*\) values in the dual-cured groups (except Un at 10,000 TCs) increased (Tables 2 and 3), which may be related to the photo-initiator camphorquinone becoming yellowish over time\(^{46}\). In the covered groups, the negative \(\Delta L^*\) values in all subgroups increased in varying degrees, which may be related to the darkening of e.max Press; however, the \(\Delta E\) value of e.max Press ranged between 0.8 and 1.2, which was regarded as color stable\(^{44}\). Also, the Es group containing a new photo-initiator Ivocerin instead of camphorquinone may increase negative \(\Delta b^*\) values. Moisture sorption of the monomers transforms the cement refractive index, and the discoloration may be partly ascribed to the hydrolysis of the molecules during aging in pure water\(^{12}\). However, manufacturers tend to hold the resin cement’s specific chemical compositions as trade secrets.

Dual-cured resin cements containing amine or amine-free self-initiators significantly influenced the resin cements’ bond strengths bonding to the glass-ceramic in accelerated aging. Thus, the second null hypothesis was rejected. Hydrofluoric acid and silane are widely used to pretreat lithium disilicate glass-ceramic because of a powerful micromechanical interlock between the ceramic and the resin-based luting agents\(^{40}\). In the present study, the \(\mu\)SBS of F2.0 was the highest and most stable among all groups at 10,000 TCs, whereas that of the other groups declined at 10,000 TCs and statistically differed from that after 24 h. The \(\mu\)SBS values after 24 h varied as follows: Un>\(V5>F2.0>\text{Es}\); at 10,000 TCs: F2.0>Un>\(V5>\text{Es}\); at 20,000 TCs: F2.0>\(V5>\text{Un}>\text{Es}\). Miyazaki et al.\(^{47}\) investigated the bond strength of resin composites on bovine dentin via in vitro research. It concluded that a positive relationship between bond strength and filler content of resin composites exists, which may be attributed to the negative correlation between cubical polymerization shrinkage and filler content. Another review also revealed that bond strength increases with the increase in filler content\(^{48}\). By the instruction of the manufacturers, the rank volume of the filler content was as follows: F2.0 (59%)>Un (42%)>\(V5 (38%)=\text{Es}\). Three silanes were used in conjunction with the corresponding resin cements in the current study. Novais et al. reported that the \(\mu\)SBS values of pure light-polymerizing resin cement were lower than those of dual-polymerizing one in light-curing mode, which could be attributed to the degree of conversion in light-polymerizing cement being lower than that of the dual-polymerizing one\(^{49}\). In addition, the degree of conversion in dual-polymerizing cement was reduced under self-curing mode compared with that under dual-curing mode. A sufficient degree of conversion ensures the best chemical and mechanical properties of resin-based materials\(^{49}\). The Es group was categorized as light-cured resin cement with one of the lowest volumes of filler content among all groups, leading to the lowest \(\mu\)SBS among all groups regardless of if after 24 h, under 10\(k\) TCs and 20\(k\) TCs accelerated aging. Meanwhile, the highest \(\mu\)SBS of F2.0 after 10,000 TCs and 20,000 TCs were ascribed to the largest volume of the filler content in all groups and as a dual-cured resin cement.

This study had some limitations. First, the specific molecular reaction mechanism of the amine-free self-initiator system was not analyzed. Second, only the 0.5 mm thickness of the ceramic slice was regarded as the lowest thickness for the assessment of color variation. Further study is needed to analyze the reaction mechanism of an amine-free self-initiator system and under multiple thicknesses of the ceramic slice.

**CONCLUSION**

Based on the limitation of this study in vitro, the
following conclusions were drawn:
1. Dual-polymerization resin cements with amine-free self-initiators exhibited comparable color stability to light-polymerization resin cements after aging via thermal cycling.
2. The $\mu$SBSs of the dual-cured resin cements with amine-free self-initiators were comparable to the conventional dual-cured resin cements, such as Unicem 200, when bonding to lithium disilicate.
3. Dual-cured resin cements with amine-free self-initiators could be an alternative for dentists when bonding high translucency porcelain restorations to teeth to obtain enhanced color stability and bond strengths.

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