The purpose of this study was to evaluate the sorption, solubility, and color stability of amine-free conventional light-cure and dual-cure resin cements and an amine-containing self-adhesive dual-cure resin cement. Sixty specimens were prepared using a light-cure resin cement (Variolink Esthetic LC, Ivoclar Vivadent; VE-LC), a dual-cure resin cement (Variolink Esthetic DC, Ivoclar Vivadent; VE-DC), and a self-adhesive dual-cure resin cement (RelyX U200, 3M ESPE; RXU200). The water sorption and solubility were tested by immersing the specimens in distilled water for 7 days. Kruskal-Wallis test was applied to the data. ΔE values of 1-day and 7-day immersion in black tea were analyzed using one-way analysis of variance followed by Tukey honest significant difference test (n = 10). There was no statistically significant difference among the groups in terms of sorption and solubility. The mean ΔE of RXU200 for the 0/1 and 0/7 days were found to be significantly lower than that of VE-LC and VE-DC (P < .05). ΔE values of the VE-LC and VE-DC groups did not reveal statistical difference. It should be taken into account that discoloration of resin cements remains a problem even with amine-free products. Int J Periodontics Restorative Dent 2021;41:e113–e120. doi: 10.11607/prd.5376

With increasing esthetic demands and improvements in dental adhesive technology, ceramic full crowns, laminate veneers, and inlays and onlays have become very popular. Resin cements provide retention and promote strength of all-ceramic restorations against fracture due to their adhesive nature.1-3

Resin cements can be categorized with respect to the bonding technique involved: total etch, bond, and resin cement; one-step etch-bond and resin cement; self-adhesive resin cement; and dual-affinity adhesive resin.4 Self-adhesive resin cements are very popular because of their advantages, such as simplifying the adhesive bonding technique, the ability to apply cement in one step, eliminating preconditioning of the tooth surface, and reducing the technical sensitivity. These cements are claimed to have bond strengths similar to conventional resin cements.5

Resin cements are also classified according to polymerization type, as self-cure, light-cure, and dual-cure. Light-cure cements are preferred because of the potential to control activation of the cement with light, which allows a longer clinical working time.6 Although light-cure cements provide better mechanical and chemical stability as a result of a higher degree of polymerization,7 dual-cure cements...
provide adequate polymerization in areas where the light cannot be reached completely.

Clinically, the luting cement is in contact with oral and sulcular fluids, causing the dissolution of resin cement, which is rapid at first and decreases in time. In addition, water sorption occurs in dental composites over time due to the hydrolytic decomposition of the bond between silane and the filler particles. Water sorption of the resin cement may cause polymer swelling, plasticization, degradation of the polymer network, reduction of tensile strength, and wear resistance. Consequently, water sorption and solubility may lead to tooth sensitivity and secondary caries (due to increased marginal leakage), failure of the cementation, and/or fracture of the restoration.

Because low- and medium-strength silica-based ceramics, which are highly translucent, require resin bonding to provide a sufficient strength, long-term color stability of the resin cement is a critical factor for its success. Because discoloring is one of the reasons esthetic restorations are replaced, resin cements are anticipated to have sufficient color stability. Discoloration of the resin cements are classified as being either intrinsic or extrinsic. Intrinsic discoloration is due to material properties, such as the type of photoinitiator and polymerization system, composition of the resin matrix, the ratio and particle size of the filler, and the degree of conversion, while extrinsic discoloration takes the form of stains caused by foods, beverages, and smoking.

Composite resins with large amounts of camphorquinone create undesirable photo-yellowing effects. Dual-cure resin cements generally contain benzoyl peroxide and aromatic tertiary amine to initiate the polymerization reaction, which leads to cement discoloration over time. Aromatic amine-benzoyl peroxide reaction generates light polymerization. A newly produced photoinitiator, Ivocerin (Ivoclar Vivadent), is claimed by the manufacturer to be resistant to color change. The literature is scarce regarding the newly produced amine-free resin cements, and there currently are no specific comparisons between light-cure and dual-cure forms of those cements with regard to water sorption, solubility, and color change.

The objectives of the present study were to evaluate the water sorption, solubility, and color stability of a new generation of conventional light-cure and a dual-cure amine-free resin cements and a self-adhesive dual-cure resin cement. The first null hypothesis tested was that the curing type and adhesive properties of resin cement had no influence on water sorption and solubility. The second null hypothesis was that the curing type and adhesive properties of resin cement had no influence on color stability.

Materials and Methods

Sixty disc-shaped specimens were prepared using a conventional light-cure resin cement (Variolink Esthetic LC, Ivoclar Vivadent; VE-LC), a dual-cure resin cement (Variolink Esthetic DC, Ivoclar Vivadent; VE-DC), and a self-adhesive dual-cure resin cement (RelyX U200, 3M ESPE; RXU200). The sample size was estimated by power analysis with G*Power software (version 3.0.10). Ten specimens were found to be enough per group to detect significant differences with 80% power and an effect size of 0.60 at a significance level of $\alpha = .05$. The manufacturer’s specifications with regard to the composition and the curing types of the cements used in this study are listed in Table 1.

VE-DC and RXU200 cements were dispensed into polytetrafluoroethylene molds, 2 mm deep and 8 mm in diameter, using an automixing dual-syringe, and VE-LC cement was dispensed from a single syringe provided by the manufacturers. A glass slab and an acetate sheet were placed on top of the mold and slightly pressed by finger to extrude the excess cement. Polymerization was carried out with a light-emitting diode unit (Valo LED, Ultradent) for 40 seconds from two opposite sides (1,000 mW/cm²). For each cement, 20 discs were manufactured. Specimen thickness was checked using a digital caliper, and any excess parts were ground away. Then, one operator (H.B.) sequentially polished one surface of all specimens using a series of polishing discs (Sof-Lex Extra-Thin, 3M ESPE) until a uniform thickness (2 mm) was obtained, which was confirmed by measuring three points on the disc. The specimens were saved in a dark environment for 7 days until they were tested.
Evaluation of the Water Sorption and Solubility

Ten specimens from each group were kept in a silica gel–containing desiccator (Model AD-6, Perkin Elmer) and weighed on an analytical balance (M1) with a precision of 0.01 mg (AUW220D, Shimadzu). Then, the specimens were stored separately in closed tubes containing 2 mL of distilled water kept at 37°C in an incubator (EN 025, Nüve) for 7 days. After the storage period, excess liquid was wiped off, and the specimens were weighed again (M2). After putting the specimens in open flasks, they were placed in the desiccator, then in the incubator at 37°C to eliminate the absorbed water. The specimens were weighed daily until they achieved a constant mass (M3). The ratios of water sorption (WS) and solubility (SI) were calculated using the formulas below:

\[
WS = 100 \times \frac{(M2 - M1)}{M1}
\]

\[
SI = 100 \times \frac{(M1 - M3)}{M1}
\]

Evaluation of Color Stability

Before colorimetric measurements, the remaining, untested specimens (n = 30; 10 per group) were washed with distilled water and gently wiped. Color measurements were made using a spectrophotometer (Ci6x NB, X-Rite). The spectrophotometer was calibrated on the docking station before the measurements. To test color stability, a black tea bag (Yellow Label Tea, Lipton) was brewed in 250 mL hot water for 3 minutes. Samples were incubated in the tea at 37°C and 100% humidity in a sealed container (to prevent evaporation) for 7 days. The tea solution was renewed daily at a standardized time. Measurements were made before immersion and at 1 and 7 days after immersion. Color change was measured and quantified by means of the CIELAB system. \(L^*\), \(a^*\), \(b^*\) parameters were determined using the spectrophotometer. \(\Delta E\) was calculated according to following formula:

\[
\Delta E = \left[ (L^1 - L^2)^2 + (a^1 - a^2)^2 + (b^1 - b^2)^2 \right]^{1/2}
\]

\(L^*\) represents the brightness, so that the greater the \(L^*\) values, the higher the brightness of the sample; \(a^*\) represents redness to greenness, so that positive values for \(a^*\) indicates redder samples and negative values indicate greener samples;

<table>
<thead>
<tr>
<th>Resin cements</th>
<th>Manufacturer</th>
<th>Product batch*</th>
<th>Shade</th>
<th>Lot no.</th>
<th>Chemical composition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variolink Esthetic LC</td>
<td>Ivoclar Vivadent</td>
<td>Light-cure (amine-free)</td>
<td>Light</td>
<td>V26525</td>
<td>UDMA and further methacrylate monomers.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>adhesive luting composite</td>
<td></td>
<td></td>
<td>Inorganic fillers: ytterbium trifluoride and spheroid mixed oxide.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Particle size: 0.04–0.2 μm (mean: 0.1 μm).</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Volume of inorganic fillers: 38%, 60–68 wt%.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ivocerin for initiator.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Additional ingredients: Stabilizers and pigments.</td>
</tr>
<tr>
<td>Variolink Esthetic DC</td>
<td>Ivoclar Vivadent</td>
<td>Dual-cure (amine-free)</td>
<td>Light</td>
<td>V17923</td>
<td>Bis-GMA, TEGDMA, methacrylate monomers containing phosphoric acid groups, stabilizer components rheologic additives, alkaline (basic) initiator components, pigments.</td>
</tr>
<tr>
<td>RelyX U200</td>
<td>3M ESPE</td>
<td>Self-adhesive dual-cure</td>
<td>A2</td>
<td>619698</td>
<td>Inorganic silanated fillers: 43 V%, 72 wt%.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(methacrylated aliphatic amine) composite cement</td>
<td></td>
<td></td>
<td>Sodium p-toluenesulfinate, camphorquinone for initiator.</td>
</tr>
</tbody>
</table>

UDMA = urethane dimethacrylate; Bis-GMA = bisphenol A glycol dimethacrylate; TEGDMA = triethylene glycol dimethacrylate.

*Information supplied by the manufacturers.
and b* represents yellowness to blueness, so that positive values for b* indicate yellower samples and negative values indicate bluer samples. L0*, a0*, and b0* signify the color coordinates before immersion (baseline) in the colorant solution; L1*, a1*, and b1* signify the color coordinates 1 day after immersion L2*, a2*, and b2* signify the color coordinates 7 days after immersion. A higher ΔE value represents a greater color difference.

Three measurements were performed for each specimen and each time point (baseline and 1 and 7 days), and the average value was calculated.

Statistical analysis was performed using SPSS software (version 22, IBM). According to Kolmogorov-Smirnov test, the water sorption and solubility data showed a non-normal distribution. Kruskal-Wallis test was then applied. The color-change data were analyzed using one-way analysis of variance. Tukey honest significant difference test was used to determine differences between groups. P values < .05 were considered statistically significant.

### Results

The median values for water sorption and solubility are shown in Table 2. With regard to water sorption (P = .07) and water solubility (P = .28), there were no statistically significant differences among the groups.

Statistical analysis of the color differences after immersion in black tea for 1 day and for 7 days are shown in Table 3.

The mean ΔE of the RXU200 for the intervals 0/1 days (between baseline and day 1) and 0/7 days (between baseline and day 7) were found to be significantly lower than that of the VE-LC (P < .001 for both 0/1 days and 0/7 days) and the VE-DC samples (P < .001 for both 0/1 days and 0/7 days). There was no statistical difference between the ΔE values of the VE-LC and VE-DC groups (P = .82 for 0/1 days and P = .46 for 0/7 days). Following immersion in the tea solution, the L* value decreased, which indicated decreased brightness. b* values increased for all groups, which signified that samples became more yellow. While the a* values for the VE-LC and the VE-DC groups decreased during the immersion period, they increased for the RXU200 group, which indicated that while VE-LC and the VE-DC groups became more green, the RXU200 group became more red.

### Discussion

Absorption of oral fluids into resin cement may adversely affect some properties of the luting cement, resulting in restoration failure. Water sorption, solubility, and color stability of amine-free conventional light-cure and dual-cure resin cements and a self-adhesive dual-cure resin cement were compared. The first null hypothesis, that the different curing types and adhesive properties of the resin cements had no influence on the water sorption and solubility, was accepted. The second null hypothesis, that the curing type and adhesive properties of the resin cements had no influence on color stability, was rejected. The RXU200 cement showed less color change than both other cements at intervals of 0/1 and 0/7 days, while VE-DC resin cement did not reveal any significant difference from VE-LC resin cement.

### Table 2 Water Sorption and Solubility of Groups

<table>
<thead>
<tr>
<th>Group</th>
<th>Water sorption, %</th>
<th>Solubility, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median</td>
<td>25th percentile</td>
</tr>
<tr>
<td>VE-LC</td>
<td>0.81</td>
<td>0.54</td>
</tr>
<tr>
<td>VE-DC</td>
<td>0.51</td>
<td>0.50</td>
</tr>
<tr>
<td>RXU200</td>
<td>0.99</td>
<td>0.51</td>
</tr>
<tr>
<td>P</td>
<td>.07</td>
<td>.28</td>
</tr>
</tbody>
</table>

Each group comprised 10 specimens. P < .05 indicates statistical significance.
With regard to sorption, it has been demonstrated that resin materials generally reached saturation within 7 to 60 days. Furthermore, with regard to solubility, it has been shown that residual unreacted monomers are released from resin materials within the first 7 days. Consequently, a 7-day immersion period was selected as the maximum time for storage, as in previous studies.

The water sorption rate of a material may be affected by the hydrophilic monomer content. It is known that bisphenol A glycol dimethacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) monomers are less hydrophobic than the urethane dimethacrylate (UDMA) monomer. However, in the present study, UDMA-containing VE-LC and VE-DC cements and Bis-GMA/TEGDMA-containing RXU200 cement did not differ statistically in terms of water sorption.

In contrast to the present results, Liu et al’s study on self-adhesive resin cements exhibited elevated water sorption and solubility values compared to conventional resin cements. Sokolowski et al investigated the stress state using water aging by means of photoelastic analysis of conventional resin cements, one of which was VE-DC, and adhesive resin cements and self-adhesive resin cements, one of which was RXU200. They reported that among all of the tested resin cements, the self-adhesive cements revealed the highest water sorption due to their acidic monomer content. Also, VE-DC cement showed a relatively high solubility value in their study. Methodologic differences might have caused the discrepancy with the present study.

Vichi et al categorized ΔE values < 1.0 as undetectable by the human eye, values between 1.0 and 3.3 were visible to skilled operators but clinically acceptable, while ΔE values > 3.3 were visible also by nonskilled persons and were deemed clinically unacceptable. In the present study, all ΔE values of the cements were above 3.3, which was considered clinically unacceptable. As several studies reported better color stability with amine-reduced, amine-free, and benzoyl peroxide-free resin cements, a lack of benzoyl peroxide in RXU200 resin cement could have a significant effect on its color stability. The amount of TEGDMA has also been reported to affect postirradiation polymerization. Because TEGDMA generates a higher initial conversion as it increases in the resin matrix, the amount of postirradiation polymerization decreases. This could have played a role in the relatively smaller discoloration of the RXU200 cement. Intensified filler content has also been correlated with improved color stability. Higher filler content (72% of weight) of the RXU200 cement compared with the other cements used in the present study might be another reason for less discoloration.

Table 3: Tukey Pairwise Comparisons of ΔE After Immersion in Black Tea

<table>
<thead>
<tr>
<th>ΔE comparison between time intervals</th>
<th>Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>VE-LC ΔE 0/1</td>
<td>4.22 ± 1.12</td>
</tr>
<tr>
<td>VE-DC ΔE 0/1</td>
<td>3.92 ± 1.21</td>
</tr>
<tr>
<td>RXU200 ΔE 0/1</td>
<td>2.18 ± 1.01</td>
</tr>
<tr>
<td>VE-LC ΔE 0/7</td>
<td>10.65 ± 1.34</td>
</tr>
<tr>
<td>VE-DC ΔE 0/7</td>
<td>9.70 ± 1.74</td>
</tr>
<tr>
<td>RXU200 ΔE 0/7</td>
<td>5.76 ± 2.15</td>
</tr>
<tr>
<td>VE-LC ΔE 1/7</td>
<td>7.21 ± 0.55</td>
</tr>
<tr>
<td>VE-DC ΔE 1/7</td>
<td>6.04 ± 1.12</td>
</tr>
<tr>
<td>RXU200 ΔE 1/7</td>
<td>4.93 ± 2.55</td>
</tr>
</tbody>
</table>

0/1 = interval of time between baseline and day 1; 0/7 = interval of time between baseline and day 7; 1/7 = interval of time between day 1 and day 7. Different superscript uppercase letters show statistical difference between the 0/1 time interval. Different superscript lowercase letters show statistical difference between the 0/7 time interval. Different superscript numbers show statistical difference between the 1/7 time interval. Each group comprised 10 specimens. *P < .05 indicates statistical significance.
Additionally, according to the color analysis, the mean $a^*$ parameter of the RXU200 group showed a tendency to be on the redder side, while that of the VE-LC and VE-DC groups showed a tendency to be on the greener side as the immersion period increased. For all groups, the $L^*$ parameters decreased, indicating that the samples became darker. For all groups, the $b^*$ parameters increased, indicating that the samples became more yellow.

In terms of the photoinitiator (Ivocerin) in the VE-LC and VE-DC cements, it is claimed by the manufacturer that no additional components are needed for radical formation. When the initiator is exposed to light, a chemical bond within the initiator molecule is broken, and two radicals are formed that then react with the monomer to produce a polymer network. Although the VE-LC and VE-DC cements used in this study were claimed by the manufacturer not to contain amines as the initiator, these cements revealed more discoloration than did the RXU200.

Mina et al$^{35}$ and Sabatini et al$^{36}$ evaluated the color change of resin composite systems for up to 1 month of water storage, and both studies stated that most of the color changes took place after initial polymerization and at the first day. In addition, they reported that only negligible color changes were subsequently found. In the present study, a significant color change was found over time for all groups. Difference of the results may have been due to the storage solution.

Silami et al$^{37}$ evaluated the color stability of resin cements used for ceramic laminate veneer bonding after accelerated aging. Light-cure cement revealed significantly higher $\Delta E$ and $\Delta L$ values than conventional dual-cure and self-adhesive dual-cure cement. That result is in harmony with the present study. Seven days of immersion in a tea solution probably simulated a period of up to 7 months of tea drinking. The $\Delta E$ value after immersion in the tea solution increased greatly as the immersion period progressed for all groups. This color change was similar with the results of previous studies.$^{38-40}$ It is known that an oxygen-inhibited layer on the specimen surface increases discoloration.$^{32}$ In the present study, the specimens’ surfaces were polished and the oxygen-inhibited layer was removed. However, in a clinical situation, the oxygen-inhibited layer exists, and that layer may exhibit more discoloration. Determining the color stability of the resin cements without use on a ceramic restoration or tooth provides more accurate results by eliminating color changes related to the other substrates.

Almeida et al$^{41}$ showed that a light-cure luting cement showed better color stability than a dual-cure cement after thermal cycles. However, in that study, ceramic cylinders were luted to enamel discs by resin cement. Because only a thin line of the luting agent is exposed to the oral environment under such circumstances, that scenario reproduces a better clinical setting than the present study.

In the oral cavity, the presence of saliva, beverages, and food and the existence of an acidic environment may affect the extent of discoloration.$^{42}$ Additionally, the effects of thermal changes in the oral cavity were not simulated in the present study. In addition, the thickness of the cement specimens (2 mm) is thicker than used in clinical circumstances, which is another limitation of this study. However, that thickness was preferred in order to reduce the effect of background color, and to provide ease of handling. Furthermore, not covering the cement with a ceramic layer can be a factor affecting color change. Future studies that focus on these factors are needed for better correlation with clinical circumstances.

Conclusions

Water sorption and solubility rates of the cements were not statistically significantly different. The discoloration of the self-adhesive dual-cure resin cement was significantly lower than that of amine-free conventional resin cements after storage in tea for 1 and 7 days. However, the discoloration was above the clinically acceptable level at day 7 for all groups. Considering the results of this study, it can be deduced that discoloration of resin cements remains a problem, even with amine-free products.

Acknowledgments

Conceptualization, methodology, sample preparation and laboratory tests, writing: F.Y. Sample preparation and laboratory tests, reviewing and editing: H.B. Reviewing and editing, validation: S.D. The authors do not
References


