Evaluation of Physical Properties and Surface Degradation of Self-adhesive Resin Cements

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This study sought to evaluate the pH value, film thickness, filler particle percentage, and morphological changes of self-adhesive resin luting cements. Products tested were G-Cem, Maxcem, Smart Cem, and RelyX™ Unicem. Cement pH was measured with pH test paper. Filler particle percentage was calculated after cement samples were incinerated at 750°C. To test film thickness, mixed cements were placed between two glass plates and compressed using a loading device. For morphological changes, specimen surfaces were observed by SEM after treatment with various media. There were significant differences among the cement pH values measured at 20 seconds after light curing, and at 90 seconds and 48 hours after mixing. Filler particle percentage was directly proportional to film thickness. Degradation of cement surfaces was also detected after surface polishing and immersion in water, acetic acid, and acetone. In conclusion, significant differences were found in the surface properties of the materials tested, and these differences might lead to differences in their clinical performance.

Keywords: Self-adhesive resin cement, Surface degradation, pH of cement

INTRODUCTION

In recent years, improvements in strength, wear resistance, marginal quality, and esthetics have led to the enormous approval of indirect esthetic restorations for a wide range of clinical applications1,2. Furthermore, the development of resin-type luting agents have served well the implementation of these indirect esthetic restorations. Resin-type luting cements provide high bond strength to restorative materials and hard dental tissues. Moreover, their useful properties of minimal solubility, stability, and biocompatibility greatly contribute to the formation of strong and durable tooth-restoration interfaces, with minimal removal of adjacent tooth tissue3,4,5.

However, adhesion of luting resin cements to processed composites has been difficult to achieve. With a view to enhancing the retention between resin cements and indirect composite restorations, surface roughening by sandblasting followed by silanation have been recommended as a predictable means6.

At the tooth surface, an adhesive system is used to bond the luting agent to the tooth substrate. Currently, all adhesives are categorized as either etch-and-rinse or self-etch adhesives8. Comparatively, a multi-step application technique is time-consuming and rather technique-sensitive. Consequently, these shortcomings may compromise bonding effectiveness9. Recently, a new type of luting cement, self-adhesive resin luting cement without surface pre-treatment10, has been introduced in the dental material market in Japan. This self-adhesive resin cement is based on a new monomer, filler and initiation technology. The manufacturer purports that the organic matrix consists of newly developed multifunctional phosphoric acid methacrylates. The phosphoric acid methacrylates can react with the basic fillers in the luting cement and the hydroxyapatite of the hard tooth tissue (RelyX Unicem, 3M ESPE, Seefeld, Germany)10.

Among the various categories of adhesive luting agents, adhesive resins and composites — incorporating adhesive monomers — are considered today to be the best luting materials11. Since the very first composite resins were developed, many efforts to improve their clinical performance have been undertaken12. Research on resin-based luting agents is mainly based on the development of new monomers13,14; while studies on the filler content focus on loading, particle size and silanation15. Such studies are of major importance because the mechanical properties of dental composites highly depend on the concentration and particle size of the filler. In particular, compressive strength, hardness, flexural strength, and elastic modulus increase with the amount of inorganic fraction, while polymerization shrinkage is said to decrease15.

Leveraging on the development of composite resins, the resin-based luting cement is an important material in dental clinical practice. Resin luting cements are popular luting agents largely because of their high physical strength and resistance against solubility. The use of resin cements in combination with dentin bonding agents can result in superior attachment of prostheses to the tooth structure. Conversely, with an incorrect use of bonding agents, resin cements have a history of producing postoperative tooth sensitivity and even pulp death16,17.
Owing to their superior bonding performance, resin-based adhesive luting materials are widely used for the cementation of inlays and onlays, crowns, posts and veneers.

Regarding conventional resin cements, we have done an investigative study on them and published a report on its findings\textsuperscript{19}. It was found that many properties of a conventional luting cement worked together to fulfill its adhesive function. In light of this finding, the characteristics of the new type of self-adhesive resin cement should similarly be examined and then compared with conventional resin luting cements. Furthermore, we also sought to confirm if morphological differences existed among the adhesive resin cements.

Therefore, the aims of this study were: (1) to investigate the pH values of selected cement materials; (2) to evaluate the weight percentage of filler particles in the four tested resin luting cements; (3) to investigate their film thickness; and (4) to morphologically analyze the cement surfaces (i.e., surface degradation) of representative samples upon treatment with various media solutions.

**MATERIALS AND METHODS**

**Materials used**

Table 1 lists the four commercially available self-adhesive resin cements tested in the present study. G-Cem (GC; GC, Tokyo, Japan, Lot No. 0612221), Maxcem Dual-cure Resin Cement (MC; Kerr Dental, Orange, USA, Lot No. 433879), Smart Cem (SC; Densply Sankin, Tokyo, Japan, Lot No. 20607B1), and RelyX\textsuperscript{TM} Unicem (UC; 3M ESPE, Seefeld, Germany, Lot No. 239545) were light- and chemically (=dual) cured resin luting cements for the adhesive insertion of indirect ceramic, composite and metal restorations. The main compositions of these materials are shown in Table 2.

**pH values of the luting cements**

The pH values of the various luting cements were measured using pH test papers (Advantec, Chiba, Japan) at room temperature (23–25°C). Measurements were done at 20 seconds after light curing using a curing light (XL3000, 3M ESPE, MN, USA), as well as at 90 seconds and 48 hours after mixing for the various self-adhesive resin cements. Measurement was done three times (n=5) on each type of luting cement, and the mean value was adopted.

**Table 1 Properties of the test materials**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Code</th>
<th>Type</th>
<th>Lot No.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-Cem</td>
<td>GC</td>
<td>Handmix</td>
<td>0612221</td>
<td>GC, Tokyo, Japan</td>
</tr>
<tr>
<td>Maxcem</td>
<td>MC</td>
<td>Automix</td>
<td>433879</td>
<td>Kerr Dental, Orange, USA</td>
</tr>
<tr>
<td>Smart Cem</td>
<td>SC</td>
<td>Automix</td>
<td>20607B1</td>
<td>Densply Sankin, Tokyo, Japan</td>
</tr>
<tr>
<td>Relyx Unicem</td>
<td>UC</td>
<td>Rotomix</td>
<td>239545</td>
<td>3M ESPE, Seefeld, Germany</td>
</tr>
</tbody>
</table>

**Table 2 Main compositions of test materials**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Main composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-Cem</td>
<td>Power: Fluoro-alumino-silicate glass, Initiator, Pigment</td>
</tr>
<tr>
<td></td>
<td>Liquid: Urethanedimethacrylate, dimethacrylate, 4-Methacryloyloxyethyl trimellitate, Distilled water, Phosphoric acid ester monomer, Silicon dioxide, Initiator, Inhibitor</td>
</tr>
<tr>
<td>Maxcem</td>
<td>Base paste: Urethanedimethacrylate, Camphoroquinone, Fluoroaluminosilicate, Other</td>
</tr>
<tr>
<td>Catalyst paste:</td>
<td>Bis-GMA, Triethyleneglycoldimethacrylate, Glycerophosphatedimethacrylate, Bariumaluminoplosilicateglass, Other</td>
</tr>
<tr>
<td>Smart Cem</td>
<td>4-Methacryloyloxyethyl trimellitate, 2-Hydroxyethyl methacrylate, Bis-GMA, Penta(methacryloyloxyethoxy) cyclophosphazene monofluoride (PEM-F), dI-Camphorquinone, Dibutylhydroxytoluene (BHT), Carbon powder, SiO\textsubscript{2}, Fe\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}, 1,3-Butanediol dimethacrylate, p-Toluenesulfonic acid sodium salt, p-Tolylidiethanolamine</td>
</tr>
<tr>
<td>RelyX\textsuperscript{TM} Unicem</td>
<td>Power: Glass power, Initiator, Silica, Substituted, Calcium hydroxide, Peroxy compound, Pigment</td>
</tr>
<tr>
<td></td>
<td>Liquid: Methacrylate multifunctional phosphoric acid ester, Dimethacrylate, Acetate, Stabiliser, Initiator</td>
</tr>
</tbody>
</table>

These material information was from manufacturer
**Weight percentage of cement particles**

Each material was tested by placing 0.3 g of it in a crucible. Samples were incinerated (30 minutes) at a high temperature of 750°C in an incinerator (AUTO FURNACE EF-I, GC, Tokyo, Japan). Weight percentage of the cement particles was determined from the weight before and after incineration.

Five samples of each type of luting cement were used for this experiment (n=5), and nominal weight was assigned to the inorganic fraction. Mean values of the data found for the luting cements were assumed to be the particle contents of the respective luting cements. This experiment followed the specification of ISO No. 4049-1978 E.

**Film thickness**

Mixing time and method for each material were done in accordance with the manufacturers’ instructions. Mixed cement was placed between two glass plates (5 mm thickness), and an indenter (2.0 mm diameter) bearing a load of 150 N was lowered slowly onto the mixed luting cement. Loading duration was 10 minutes.

Specimen thickness was measured using a digital thickness measuring instrument (DIGIMICRO, MS-11C, Nikon, Tokyo, Japan). Cement film thickness was then derived from the difference in cement thickness before and after loading. Measurements were done at room temperature (23−25°C) and repeated five times for each material (n=5). This experiment followed the specification of ISO 9917[10].

**Statistical analysis**

Mean values of the different data groups for the different materials were compared using one-way ANOVA and Tukey’s HSD multiple comparison test at a significance level of 0.05. All statistical calculations were performed using a statistics software package (SPSS 10J for Windows, SPSS Japan Inc., Tokyo, Japan).

**Morphological analysis of the cement surfaces**

Specimens were shaped in the form of a disk with a diameter of 10 mm and a thickness of 1 mm. Specimens were made from mixed cements that had been light-cured for 20 seconds using Curing Light. One of the following four surface treatments were then applied to each specimen disk: (A) surface polishing with #600 to #1200 diamond grinding disks (Struers A/S, Copenhagen, Denmark); (B) storage in distilled water for 90 days (37°C) after surface polishing; (C) immersion in acetic acid for 12 hours; or (D) immersion in ultrasound acetone bath for five minutes.

Subsequently, these surface-treated cement specimens were observed using a scanning electron microscope (SEM; S-2300, Hitachi, Tokyo, Japan) for morphological changes.

**RESULTS**

**pH values of the luting cements**

Table 3 shows the pH results of the various resin luting cements. At 20 seconds after light curing, the pH values were 5.0 (UC) or less (GC: pH 2.0; MC: pH 2.2; SC: pH 3.6). At 90 seconds after cement mixing, the pH value were 3.6 (SC) or less (GC: pH 1.8; MC: pH 2.0; UC: pH 2.8). At 48 hours after cement mixing, the pH values were pH 4 (SC) or less (GC: pH 3.6; MC: pH 2.4), with the exception of UC (pH 7.0).

**Weight percentage of cement particles**

Figure 1 shows the mean values and standard deviations of the weight percentages of cement particles. They ranged from 60.7% for GC to 70.6% for UC. MC and SC ranged between 60% and 70%, with MC at 68.2% and SC at 65.7%. There were no significant differences among MC, SC, and UC (P<0.05). However, there were statistically significant differences in particle content between GC and the other three cements (MC, SC, and UC) (P<0.05).

**Film thickness**

Film thickness was obtained using the test method described in ISO 9917. Measurements obtained in Fig. 1 showed that film thickness was greatest for MC (25.7 μm), followed by UC (23.2 μm).

![Graph showing weight percentages of particles (bar chart) and film thickness values (line chart) of the self-adhesive luting cements.](image-url)
Fig. 2  SEM images of G-Cem specimen surface: (A) surface-polished condition; (B) storage in water for 90 days; (C) acetic acid surface treatment condition; and (D) acetone surface treatment condition (original photograph magnification ×5000; thumbnail ×1000).

Fig. 3  SEM images of Maxcem specimen surface: (A) surface-polished condition; (B) storage in water for 90 days; (C) acetic acid surface treatment condition; and (D) acetone surface treatment condition (original photograph magnification ×5000; thumbnail ×1000).
Fig. 4  SEM images of Smart Cem specimen surface: (A) surface-polished condition; (B) storage in water for 90 days; (C) acetic acid surface treatment condition; and (D) acetone surface treatment condition (original photograph magnification ×5000; thumbnail ×1000).

Fig. 5  SEM images of Unicem specimen surface: (A) surface-polished condition; (B) storage in water for 90 days; (C) acetic acid surface treatment condition; and (D) acetone surface treatment condition (original photograph magnification ×5000; thumbnail ×1000).
SC (18.4 μm), and GC (14.3 μm). It could be seen that cements with a high content of particles tended to yield thicker films, and there were no significant differences among MC, SC, and UC (P<0.05). However, there were statistically significant differences between GC and the other three cements (MC, SC, and UC) (P<0.05).

Morphological analysis of the cement surfaces
The SEM images suggested some differences between GC (Fig. 2), MC (Fig. 3), SC (Fig. 4) and UC (Fig. 5). Surface degradation was observed for all the treatment conditions — namely, surface polishing, storage in water; acetic acid treatment, and acetone treatment. Cement particles fell away as observed in the GC specimens in all treatment conditions. Moreover, decomposition of the luting cement matrix was observed in the GC, MC, and SC samples after being subjected to acetone treatment (i.e., organic solvent).

In the MC samples, surface degradation was clearly present after water storage (Fig. 3B). As for SC, surface degradation was clearly present after water storage and acetic acid treatment (Figs. 4B and 4C); decomposition of the luting cement matrix was also clearly observed after acetone treatment (Fig. 4D). UC underwent surface degradation only when immersed in acetic acid (Fig. 5C).

Except for SC (Fig. 4), the inorganic fillers of the tested resin cements were composed of universal or microfiller particles of an indeterminate form. Particle size in all the four cements was less than 5 μm, ranging mostly between 2 and 3 μm.

DISCUSSION
In the recent years, the self-adhesive resin cement used to the study was developed following the invention of fluoride-releasing luting cement. Self-adhesive resin cements are also called auto-adhesive luting cement. A distinctive advantage of self-adhesive resin cements lies in the saving of chair-side time due to reduced application steps. Traditional resin luting cements require an acid or primer to process the tooth surface so as to achieve the adhesive effect. By contrast, the phosphoric acid ester monomer is included in self-adhesive resin luting cements to perform the etching step. This meant that self-adhesive resin cements directly etch the tooth surface without the additional step of acid or primer treatment.

When restoring large tooth defects, indirect composite restorations are a preferred option because of several advantages. These advantages include better marginal adaptation and anatomic form, more resistance to wear, increased fracture resistance, and more control of polymerization shrinkage. At this juncture then, it must be highlighted that cements are indispensable for luting these indirect restorations at the dental clinic.

The longevity of an indirect composite restoration is influenced by the physical and mechanical properties of both the restoration and the luting agent. Nonetheless, the key factor is the bonding efficacy at the tooth-restoration junction. Pertaining to bonding efficacy at the interface, variations in cement composition may influence the adhesive properties.

pH values of the cements
The pH values of the tested self-adhesive resin cements were lower than 4 (pH<4) at 90 seconds after mixing. GC had the lowest pH (pH 1.8) while SC had the highest (pH 3.6). Such low pH values allow the etching of enamel and dentin. However, at 48 hours after mixing, GC, MC, and SC still had pH values less than 4, but not for UC (pH 7.0). It is noteworthy that with the exception of UC, the latter pH values were slightly higher than the 90-second specimens as well as those at 20 seconds after light curing. Such low pH values after light irradiation yield a positive effect on restoration bonding.

However, the traditional acid-base reaction glass polyalkenoate (glass ionomer) cement almost reached neutral pH (pH>5.0) at 24 hours after mixing. While a low pH is useful for the etching of the enamel and dentin to be performed immediately after mixing, it was speculated that if a low pH condition were maintained for too long a time, it might adversely influence the adhesion of mixed cement to the tooth structure.

Weight percentage of cement particles
Many factors influence the degradation and wear resistance of dental composites. The effect of filler volume on wear resistance follows a linear relationship. In our study, the luting cement particle content had almost the same percentage range (65–70%), except for GC (60.7%). UC (70.6%) showed the highest percentage of filler particles among the tested resin luting cements. Conversely, the particle percentage of GC was significantly lower than those of the other tested luting cements. An increase in particle content theoretically leads to an increase in viscosity. However, the tactile feel of UC during the current in vitro test was the same as that for the other cements. In other words, viscosity did not seem to be increased in UC.

Manufacturers generally claim that restorative materials with increased filler particle percentage possess better physical and mechanical properties. In the same vein, an optimal dental restorative material should also mimic the structural, mechanical, and physical characteristics of dentin and enamel. Therefore, a good luting cement is expected to
posses good adhesive property as well as high physical properties. In this study, UC seemed to fulfill all these requirements, unlike the other tested resin luting cements.

**Film thickness**

In dental clinical practice, it is very important for the clinician to understand the properties of the luting cement. The conventional tests for testing the properties of a luting cement are the film thickness test and the viscosity test, whereby their typical specifications are outlined ISO 9917. Clinicians tend to use these test data when selecting luting cement materials as well as with due consideration to the handling property of the cement. However, no standardization exercise has not been done for resin luting cements. Therefore, in the reports of Levin and Van Meerbeek et al., film thickness and consistency of the resin luting cements were examined using standard methods employed for other cements.

In the context of the present study, GC — with the lowest particle percentage — also yielded the lowest value for film thickness. For the other three tested luting cements, film thickness was directly proportional to particle percentage. There had better be much content of a particle, if acquire the character with a good film thickness and fluidity.

**Morphological analysis of the cement surface**

Resin composites are generally composed of silanized silicate glass fillers in a polymeric matrix derived from the polymerization of a mixture of methacrylate monomers. For self-adhesive resin cements, their compositions — and hence their properties — bear a close resemblance to composite resins (Table 2).

All the tested luting cements had one common characteristic: they all contained the phosphoric acid ester monomer. As for the matrices of GC, MC, SC, and UC, the main ingredient was resin. However, for UC, glass ionomer cement (particles) was also included in the ingredients (Table 2), which meant that some characteristics of glass ionomer cement were inevitably reflected to a certain extent.

In the aspect of surface degradation, differences were observed among the different treatments of water storage, acetic acid and acetone immersion. Then, among the tested materials, more particles fell away and more pronounced matrix decomposition was observed in GC, MC, and SC. In addition, these phenomena (i.e., the falling away of cement particles and the decomposition of matrix component) were observed more clearly in the samples which were immersed in acetic acid (Figs. 2C, 3C, 4C, 5C). It was thought that these phenomena occurred due to the decomposition of the hydrophilic component of the cement matrix. Another possible explanation was the weak bonding between the cement particles and the matrix resin. The latter phenomenon could be caused by the high susceptibility of fluoroaluminosilicate to moisture. The base resin contained many ingredients which were easily hydrolyzed, such as urethanedimethacrylate, dimethacrylate, and 4-methacryloyloxyethyl trimellitate. Consequently, the adhesion of the particles to the matrix was destroyed by hydrolysis.

Based on the SEM images, there seemed to be a loss of particles. Ideally, the interfacial bond can form a continuous stress distribution between the particles and the matrix resin, provided that the coupling agent has properties intermediate to those of the particles and those of the matrix. On this note, the composite resin has another advantage when used as the coupling agent in dental composites: it protects, at least to some extent, the filler against hydrolytic degradation. However, cements particles complicate matters such that filler surface treatment by silane cannot be easily done. As a result, at the part of the organic matrix where there was insufficient polymerization, it would be dissolved by acetone and the particles easily fell away (Figs. 2D, 3D, 4D).

When acetone was used to treat the resin luting cements, the strongest surface degradation occurred in GC, followed by MC and SC. UC proved to be the most stable under acetone surface treatment. This seemed to be related to the stability of the matrix resin and the particle content (70%) of UC. However, the falling away of particles was confirmed in UC (Fig. 5C) under acetic acid treatment. This seemed to have occurred because the particles in the core of the cement were more susceptible to the effects of acetic acid.

Meanwhile, there are two types of self-adhesive resin cements: handmix versus automatic. In the handmix system, the cement might be not evenly mixed and that air bubbles might be entrapped in the resin cement material. In the automatic system, the cement paste might not be thoroughly mixed as the mixing was constrained and limited by the length of the nozzle. To find out more about the influence of cement mix type on the physical properties of self-adhesive resin cements, a research program on this subject will be implemented in the future.

**CONCLUSIONS**

In this study, a series of tests were performed with a view to examining and comparing the physical properties and morphology of four cement materials.

Based on the results obtained for pH, particle content, film thickness, and surface morphology, there were significant differences in the tested properties among the four self-adhesive resin cements. The physical properties of a self-adhesive resin luting
cement play a very important role in clinical applications. Results of this study seemed to suggest that self-adhesive resin cements are beneficial for indirect restorations in the dental clinic when compared against conventional luting cements.

ACKNOWLEDGEMENTS

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