Influence of Curing Method and Storage Condition on Microhardness of Dual-cure Resin Cements

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This study evaluated the influence of curing method and storage condition on the microhardness of dual-cure resin cements: Panavia F 2.0 (PF) and Nexus 2 (NX). The specimens were either light-cured (LC) or chemically cured in darkness (CC). After 24 hours of storage in dry chamber (Dry) or distilled water (DW), the specimens were sectioned and polished. The microhardness of resin cement matrix was measured using a nanoindentation tester (ENT-1100). The data (n=6) were statistically analyzed with t-test, two-way ANOVA (p<0.05), and Tukey HSD test (α = 0.05). It was found that the factors of curing method and storage condition had significant effect on microhardness. For both PF and NX, LC presented higher microhardness than CC, while DW showed higher microhardness than Dry. In conclusion, dual-cure resin cements could achieve high degree of cure when light-cured. In addition, the microhardness of the resin cements evaluated did not decrease when kept in water.

Key words: Resin cement, Microhardness, Storage condition, Curing method

INTRODUCTION

Recently, resin cements have been extensively used and marketed due to the increasing demand for optimum and high-quality esthetic restorations. When compared to conventional cements such as zinc phosphate cement¹, polycarboxylate cement or glass-ionomer cement², resin cements are a preferred choice because of their mechanical properties. If proper pretreatment is duly performed, resin cements bond not only to tooth structures³,⁴, but also to metal and porcelain³,⁵,⁶.

In particular, porcelain and resin composite are used commonly as tooth-colored restorative materials. Since these materials are brittle, it is imperative that bonding between restoration and tooth is reinforced with good adhesive. Since light can penetrate through such tooth-colored materials, dual-cure resin cements are routinely used for the adhesion of such esthetic indirect restorative materials. Dual-cure resin cements can be polymerized by both self-cure and photo-cure initiators⁷⁻¹¹. With light curing, dual-cure resin cements demonstrate good mechanical properties and optimal degree of conversion at the early stages of hardening¹². Therefore, dual-cured resin cements are able to achieve significantly higher bond strength than chemically-cured resin cement immediately after light curing¹³. However, the bonding durability of resin cement is affected by the amount of light received by the cement¹⁴,¹⁵. It was reported that light attenuation is caused by air, dentin, enamel, and restoration¹⁶.

Dual-cure resin cements are composed of an organic resin cement matrix (such as Bis-GMA or urethane dimethacrylate resin) and inorganic filler particles. As filler particles are relatively larger than the indenter of conventional microhardness testing machines, data obtained from usual microhardness tests are prone to reflect prominently the type and content of the filler particles¹⁷. Therefore, to evaluate the curing ability of a dual-cure resin cement, it would be more appropriate to measure the microhardness of the organic resin cement matrix. However, the microhardness may be affected by water absorption because resin cement is exposed to saliva after cementation in clinical situations.

Against this backdrop, this study sought to investigate the influence of curing method and storage condition on the microhardness of organic resin cement matrix — of two commercially available dual-cure resin cements — using the nanoindentation technique. The null hypothesis tested was that curing method and storage condition would not affect the microhardness of the organic matrix of dual-cure resin cements.

MATERIALS AND METHODS

Dual-cure resin cements used in this study

The product name, manufacturer, batch number, and basic composition of each dual-cure resin cement used in this study are listed in Table 1. Two commercially available dual-cure resin cements, Panavia F 2.0 (PF, Kuraray Medical, Tokyo, Japan) and Nexus 2 (NX, Kerr, Orange CA, USA), were evaluated. Both cements consisted of two paste materials. For PF,
Paste A included an acidic monomer, MDP (methacryloxydecyl dihydrogen phosphate), and Paste B included NaF which releases fluoride to help prevent secondary caries around restorations 6). Its filler particle loading was 78 wt.%. NX was a Bis-GMA-based universal resin cement which contained 70 wt.% inorganic filler particles with an average particle size of 0.6 microns.

**Specimen preparation**

The specimen preparation methodology is illustrated in Fig.1. Same amount of two paste materials of each resin cement were dispensed and mixed together in accordance with manufacturer's instructions. A split mold (0.4-mm thickness × 4-mm diameter) was made with a vinyl tape (Yamato, Tokyo, Japan) on a plastic matrix strip (Lumi Strip, Inoue Attachment Co., Tokyo, Japan) placed on top of a dentin slice, which served as the background as in a clinical situation 7. The mixed cement was filled into the mold and then covered with another plastic matrix strip, and gently pressed to obtain a flat surface.

The specimens were divided into two groups. For the first group, the specimens were light-cured from the top surface for 20 seconds using a visible light-curing unit, Candishlux (J Morita, Kyoto, Japan) (LC). Light irradiation time was set according to manufacturer's recommendation. For the other group, the specimens were left in darkness for 15 minutes at room temperature (CC). Following which, all specimens were removed from the mold and stored individually in glass containers either without water (Dry) or with 10 ml of distilled water (DW). The samples were kept at 37°C for 24 hours enclosed in a dark box to avoid additional light exposure from environment. When the specimens were removed from glass containers, they were vertically sectioned into halves at the center of the disk using a razor blade. The sectioned specimens were then embedded in self-curing epoxy resin (EPON815, Nissin EM Co. Ltd., Tokyo, Japan) for one day. After epoxy resin was cured, the surface was ground with waterproof silicon carbide papers (grit size: #600, #800, #1000, #1200, and #1500; Marumoto Struers KK, Tokyo, Japan) under running water and polished with diamond pastes (DP-Paste; particle size: 6, 3, 1, and 0.25 μm; P. Struers A/S, Ballerup, Denmark) to obtain mirror-like surface. After polishing with each grit size, debris on the polished surface was removed by ultrasonic cleaning in distilled water.

Table 1: Resin cements tested

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer (Batch Number)</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANAVIA F 2.0</td>
<td>Kuraray Medical Inc., Tokyo, Japan (T000410)</td>
<td>Paste A: Quartz glass, microfiller, MDP, methacrylates, photoinitiator; Paste B: Barium glass, NaF, methacrylates, chemical initiator</td>
</tr>
<tr>
<td>NEXUS 2</td>
<td>Kerr Co., Orange CA, USA (210225)</td>
<td>Base: Bis-GMA, Camphoroquinone, Barium alumino-boro-silicate glass; Catalyst: Bis-GMA, Triethylene glycol dimethacrylate, Barium alumino-boro-silicate glass</td>
</tr>
</tbody>
</table>

**Fig.1 Schematic illustration of the methodology of specimen preparation.**
for five minutes.

**Microhardness measurement**

The microhardness measurement methodology is illustrated in Fig. 2. The nanoindentation hardness test was performed using a nanoindentation testing machine (ENT-1100, Elionix, Tokyo, Japan). The nanoindentation testing machine apparatus consisted of three major components: a triangular pyramidal diamond indenter, a CCD camera, and a movable test stage that transported the specimen between the CCD camera and the indenter. These components were placed in an isolated enclosure with a temperature controller on an anti-vibration isolator to exclude environment-related influences such as room temperature, floor vibration, and noise. Z-axis displacement was measured by a capacitive displacement. Loading control system was powered by electromagnetic force. The loading force for indentation was 0.05 N – which was thus determined based on previous studies.17,18

The samples were gently air-dried and mounted with the polished side up – in a heated modeling compound – on the stage of the nanoindentation testing machine. Observing the sample with a CCD camera, seven indentation points on the matrix were individually selected and programmed for each specimen. The first measurement was made approximately 500 μm from the specimen’s lateral side and at the center from the upper and lower surfaces of the cross-sectioned disk of the cement. A distance of 50 0 μm was maintained between each measurement. After each measurement, the geometry of the indentation mark would be verified on the attached display to confirm that testing was not done on a filler particle. If it was so, the measurement would be discarded. The microhardness value of each measurement was calculated by an attached computer. Then, for each specimen, microhardness value was determined by calculating the average value of all seven measurements.

**Statistical analysis**

A total of 48 specimens were divided into eight groups of six specimens each. All microhardness data were analyzed statistically among the two resin cements with t-test. Then treating each cement as an independent experiment, the microhardness data were analyzed by two-way analysis of variance. The two factors analyzed were curing method and storage condition. Following this, the microhardness data of PF were analyzed using t-test. As for NX, multiple comparisons of microhardness data were conducted using Tukey HSD test (α = .05). Statistical significance in all analyses was set at 5% probability level. The data were analyzed using Statistical Package for Medical Science (Dr. SPSS II for Windows) software.

**RESULTS**

The statistical analysis using t-test revealed significant difference in microhardness between PF and NX (t=3.750, p=0.001). The boxplot graph of microhardness is shown in Fig. 3.

As for the microhardness results of each resin cement, they are shown in Tables 2 and 3.

Regarding PF, two-way ANOVA revealed that the factors of curing method (F=9.348, p=0.0062)
Table 2 Microhardness of PF (Mean±S.D.: kgf/mm², n=6)  

<table>
<thead>
<tr>
<th>Material</th>
<th>LC</th>
<th>CC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>49.95±11.23a</td>
<td>31.68±6.19b</td>
</tr>
<tr>
<td>DW</td>
<td>68.96±7.46A</td>
<td>57.35±7.73bA</td>
</tr>
</tbody>
</table>

Same superscript indicates significant differences (p<0.05)

Table 3 Microhardness of NX (Mean±S.D.: kgf/mm², n=6)  

<table>
<thead>
<tr>
<th>Material</th>
<th>LC</th>
<th>CC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>41.27±1.55a</td>
<td>24.73±3.48</td>
</tr>
<tr>
<td>DW</td>
<td>43.90±1.80A</td>
<td>35.41±1.30</td>
</tr>
</tbody>
</table>

Same superscript indicates no significant differences (p>0.05)

and storage condition (F=61.812, p<0.0001) had significant effect on microhardness. However, there were no significant interactions between them (F=0.117, p=0.7356). The results of t-test further revealed the following. For Lux LC and CC, DW showed significantly higher value than Dry (t=5.090, p=0.000; t=6.350, p=0.000, respectively). For DW, LC showed a significantly higher value than CC (t=2.647, p=0.024). However for Dry, LC and CC showed no significant differences (t=1.771, p=0.107).

Regarding NX, not only did both factors of curing method (F=193.022, p<0.0001) and storage condition (F=54.545, p<0.0001) show significant effect on microhardness, there was also a significant interaction between them (F=19.933, p=0.0002). Multiple comparison tests using Tukey HSD revealed that there were significant differences between all of the groups except between DW and Dry in LC group.

**DISCUSSION**

The nanoindentation technique is a special hardness testing method. It has several advantages for microhardness determination, such as precise positioning up to maximum indentation depth of about 20 μm and load resolution of approximately 0.2 μN.

Previously, the nanoindentation technique has been used in dentistry to measure the microhardness of very narrow regions, such as resin-dentin bonding area^{9,20}, dentin-enamel junction^{21}, caries-affected dentin^{22}, and filler particles of dental restorative materials^{23}. In this study, this technique was used to evaluate the influence of two curing methods and two different storage conditions on the microhardness of organic resin matrix of two dual-cure resin cements.

It is believed that the hardness value of a cured resin matrix well reflects the degree of conversion. This is because the mechanical properties of a polymer depend on the cross-linking density and quality of the network – which forms during polymerization^{24}. Therefore, the hardness value has been used as an indicator to check the degree of cure of polymers.

In this study, two curing methods – light-curing and chemical-curing – were compared because the intensity of the light reaching the cement is not always sufficient in clinical situations. As the thickness of a restoration increases, the hardness is reduced due to reduced light intensity through the restoration^{25-27}. In addition, resin composites are much less capable in transmitting light than ceramic materials even in the same shade^{28}. Moreover, resin cements are used for luting metal restorations and endodontic posts^{29} – which are impervious to light transmission. In such clinical cases, the main curing method employed is chemical curing.

In both PF and NX, LC presented higher microhardness value than CC. This finding strongly supported the notion that dual-cure resin cements could achieve higher degree of cure if light-cured, as compared to chemical curing only. Rugeberg et al.^{30} investigated the influence of light exposure on polymerization of dual-cure resin cements using infrared spectroscopy. They observed distinct differences in the degree of cure of resin cements cured with and without light, and revealed that dual-cured resin cements depended on photoactivation to achieve an optimum degree of monomer conversion^{30}. On the other hand, chemical curing alone is insufficient for dual-cure resin cements to achieve maximum degree of hardening^{31,32}. In addition, the degree of hardening achieved through chemical curing varies among the cements^{33,34}.

It was expected that DW specimens would demonstrate lower microhardness than the Dry specimens due to water uptake by the cement matrix. However, the DW specimens showed a higher microhardness value than the Dry specimens except for LC of NX. The DW specimens were stored in distilled water for one day, while the Dry specimens were stored for one day without water. After embedding in epoxy resin, the surfaces of the specimens were polished under running water. Although this contact with water could have influenced the results,
especially for the Dry specimens, this period of polishing was too short for significant water uptake. Therefore, the influence of water during specimen preparation on microhardness was negligible. Rather, water sorption and solubility of composite materials significantly increase along time up to seven days\(^\text{31}\).

It is well known that oxygen inhibits resin matrix polymerization\(^\text{30}\). In this study, water storage may have acted as an air barrier, thus enhancing the polymerization of the cement matrix. Phanthavong et al.\(^\text{37}\) reported the same tendency in one-step adhesive systems where the microhardness of specimens stored in distilled water was significantly higher than that of dry specimens. They suggested that the ensuing acid-base reaction and cross-linking of polymers would continue after initial polymerization under presence of water. In this study, this phenomenon could have occurred in acidic monomer-containing resin cement, PF. Ruegggeberg and Craig\(^\text{35}\) reported that a light-cured composite showed higher microhardness when stored in distilled water compared to that in dry condition. They pointed out that water sorption was a poor predictor for the degree of monomer conversion. Resin is known to be sensitive to moisture during application, which could lead to poor clinical results\(^\text{30}\). However, the present results suggested that the microhardness of organic resin cement matrix might not be adversely affected by exposure to moisture in saliva immediately after cementation. In addition, the reason remained unclear why there were no differences in microhardness between DW and Dry in LC of NX in the present study.

According to the present results, the null hypothesis was accepted. Previous studies have reported some clinical factors influencing the polymerization of resin-based materials\(^\text{37}\). Care should be taken not to trap any air bubbles when mixing two-paste type resin cements. Air bubbles in cement matrix not only inhibit polymerization of the cement, but also become a defect in the cement after polymerization. Light curing should be done from several directions to increase the opportunity for light curing. Clinically, the cavity is applied with some pretreatment solution for bonding with resin cement. It was reported that components of a self-etching primer attached to the resin cement did influence the polymerization of resin cement matrix\(^\text{30}\).

The quartz-tungsten halogen lamp, which is the most commonly used light-curing unit, was used in this study. However, some new light-curing units, such as plasma-arc, high-power halogen, high-power LED, have been introduced in the market\(^\text{14,37,39}\). Tashiro et al.\(^\text{30}\) suggested that the irradiation time through a composite could be shortened if a high-intensity light curing unit is used. Moreover, when Tashiro et al increased the irradiation time with a high-intensity light unit, the immediate dentin bonding strength was remarkably improved\(^\text{39}\).

Further studies should be carried out to verify the effects of long-term storage, tooth structure conditioning, and different light curing units on the mechanical properties of dual-cure resin cements.

REFERENCES


