Influence of Light Irradiation Through Zirconia on the Degree of Conversion of Composite Cements

Masanao Inokoshi\textsuperscript{a} / Pong Pongprueksa\textsuperscript{b} / Jan De Munck\textsuperscript{c} / Fei Zhang\textsuperscript{d} / Kim Vanmeensel\textsuperscript{e} / Shunsuke Minakuchi\textsuperscript{f} / Jozef Vleugels\textsuperscript{g} / Ignace Naerth\textsuperscript{h} / Bart Van Meerbeek\textsuperscript{i}

Purpose: To assess the light irradiance (LI) delivered by two light-curing units and to measure the degree of conversion (DC) of three composite cements and one flowable composite when cured through zirconia or ceramic-veneered zirconia plates with different thicknesses.

Materials and Methods: Three dual-curing composite cements (Clearfil Esthetic Cement, Panavia F2.0, G-CEM LinkAce) and one light-curing flowable composite (G-aenial Universal Flo) were investigated. Nine different kinds of zirconia plates were prepared from three zirconia grades (YSZ: Aadva and KATANA; Ce-TZP/Al\textsubscript{2}O\textsubscript{3}: NANOZR) in three different thicknesses (0.5- and 1.5-mm-thick zirconia, and 0.5-mm-thick zirconia veneered with a 1.0-mm-thick veneering ceramic). Portions of the mixed composite cements and the flowable composite were placed on a light spectrometer to measure LI while being light cured through the zirconia plates for 40 s using two light-curing units (n = 5). After light curing, micro-Raman spectra of the composite films were acquired to determine DC at 5 and 10 min, 1 and 24 h, and at 1 week.

Results: The zirconia grade and the thickness of the zirconia/veneered zirconia plates significantly decreased LI. Increased LI did not increase DC. Only the Ce-TZP/Al\textsubscript{2}O\textsubscript{3} (NANOZR) zirconia was too opaque to allow sufficient light transmission and resulted in significantly lower DC.

Conclusion: Although zirconia-based restorations attenuate the LI of light-curing units, the composite cements and the flowable composite could be light cured through the YSZ zirconia. LI is too low through Ce-TZP/Al\textsubscript{2}O\textsubscript{3} zirconia, necessitating the use of self-/dual-curing composite cements.

Keywords: zirconia, degree of conversion, micro-Raman, light spectrometer, light-curing unit, composite cement.

Zirconia ceramics have now successfully been used in dentistry for about a decade. They are employed not only as frameworks for all-ceramic crowns and bridges, on which a veneering ceramic is fired to achieve individualized characterization, but more recently also as monolithic “full-contour” zirconia restorations.\textsuperscript{7,8,15} Chiefly due to its high chemical inertness, one of the major limitations of dental zirconia remains the difficulty of bonding it to residual tooth structure. If fully achievable, bondable zirconia would obviously limit the need for macroretention and thus enable less invasive tooth preparation.\textsuperscript{33} A recent systematic review on bonding to zirconia revealed that the currently most
effective and durable zirconia-bonding protocol involves me-
chanical pre-treatment of the zirconia surface using tribo-
chemical silica sandblasting, followed by chemical pre-treat-
ment with a combined 10-MDP/silane primer prior to the
actual luting process using a hydrophobic composite ce-
ment.\textsuperscript{13} Thanks to such improved zirconia-luting proced-
ures, composite cements may become the first-choice ce-
ments to lute zirconia-based restorations in the future, re-
placing conventional glass-ionomer cements that are still
used today for standard conventional cementation.

Based on the mode of polymerization initiation, compos-
ite cements can be classified as 1. two-component chem-
ical or self-curing composite cements; 2. two-component
dual-curing composite cements (curing both chemically and
by light); 3. one-component solely light-curing composite
cements. While the latter composite cements are typically
used when cementing porcelain veneers that are thin and
transparent enough to transmit light, dual-curing composite
cements are indicated for thicker, more opaque, most often
posterior restorations, so that the cements also adequately
cure in areas largely inaccessible for light.\textsuperscript{3} While having
self-curing potential, some recent studies revealed that
dual-curing composite cements also benefit from additional
light curing and can thus reach a higher DC.\textsuperscript{20,21}

Zirconia-based fixed dental prostheses (FDPs) are very
opaque, which significantly reduces the LI delivered by light-
curing devices when used to cure the composite cement
through the restoration. This lower LI has previously been
shown to result in decreased DC, significantly affecting the
mechanical properties of the cement and its resultant
bond.\textsuperscript{16} A new trend in dental zirconia technology involves
the development of full-contour zirconia, primarily to im-
prove the mechanical properties as a monolithic restoration
and to avoid chipping of the veneering ceramic that is today
reported to have a prevalence of about 10\% to 33\%.\textsuperscript{24,28} At
the same time, new zirconia formulations are more trans-
lucent, which directly improves the esthetic outcome and al-
lows better light transmission, enabling light-curing luting
options. To date, however, hardly any data are available
with regard to the (light-)curing potential of composite ce-
ments when used to lute zirconia-based restorations.

Therefore, the objectives of this study were 1. to evalu-
ate the effect of zirconia, varying in kind and thickness, on
the transmittance of light in terms of LI, and 2. to measure
the DC of three different dual-curing composite cements and
one solely light-curing flowable composite that can be
used as a composite cement. The null hypotheses tested
were that 1. LI delivered by two light-curing units and 2. DC
of the composite cements and the flowable composite were
not affected by the kind and thickness of zirconia.

**MATERIALS AND METHODS**

**Specimen Preparation**

To simulate a clinical luting procedure for zirconia-based
restorations, nine zirconia plates (1.0 × 1.0 cm) were pre-
pared from three zirconia grades – two yttria-stabilized zirco-
nias (YSZ), Aadva (GC; Tokyo, Japan) and KATANA (Kuraray
Noritake; Tokyo, Japan), and one ceria-stabilized tetragonal
zirconia polycrystal/alumina (Ce-TZP/Al\textsubscript{2}O\textsubscript{3}): NANOZR (Pana-
sonic; Osaka, Japan) – in three different thicknesses, 0.5-
and 1.5-mm-thick zirconia, and 0.5-mm-thick zirconia ve-
neered with a 1.0-mm-thick veneering ceramic. The zirconia
material details are summarized in Table 1. Portions of the
three composite cements and one flowable composite
(Table 2) were each placed on a 1-mm-thick transparent
microscope slide (Gerhard Menzel; Braunschweig, Germany)
and squeezed to a film thickness of about 100 μm using a
microscope coverslip positioned on top, with two other cov-
erslips positioned one on each side of the composite por-
tion, serving as a spacer. The resultant diameter of the
composite specimens was approximately 5 mm. The top
coverslip was kept in position throughout the whole exper-
iment to avoid oxygen inhibition. The complete study design
is presented schematically in Fig 1.
Table 1  Overview of the three zirconia grades investigated and the different zirconia/veneered zirconia plate configurations

<table>
<thead>
<tr>
<th>Zirconia plate</th>
<th>Zirconia type</th>
<th>Plate thickness</th>
<th>Preparation</th>
<th>Clinical relevance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aadva (GC)</td>
<td>YSZ</td>
<td>0.5 mm</td>
<td>Fully sintered Aadva plate (1.0 × 1.0 cm) provided by manufacturer.</td>
<td>Simulates the cervical margin of a YSZ zirconia restoration.</td>
</tr>
<tr>
<td>Aadva + Initial Zr-FS (GC)</td>
<td>YSZ</td>
<td>0.5 + 1.0 mm</td>
<td>Fully sintered Aadva plate (1.0 × 1.0 cm) provided by manufacturer. The veneering ceramic (Frame Modifier, FD91, DA2 CL-F and E) was fired by an experienced dental technician.</td>
<td>Simulates the occlusal part of a ceramic-veneered YSZ zirconia restoration.</td>
</tr>
<tr>
<td>AadvaEI (GC)</td>
<td>Full-contour YSZ</td>
<td>1.5 mm</td>
<td>Fully sintered AadvaEI plate (1.0 × 1.0 cm) provided by manufacturer.</td>
<td>Simulates the occlusal part of a full-contour zirconia restoration.</td>
</tr>
<tr>
<td>KATANA HT (Kuraray Noritake)</td>
<td>Colored YSZ</td>
<td>0.5 mm</td>
<td>Fully sintered KATANA HT plate (1.0 × 1.0 cm) provided by manufacturer.</td>
<td>Simulates the cervical margin of a YSZ zirconia restoration.</td>
</tr>
<tr>
<td>KATANA HT + Cerabien ZR (Kuraray Noritake)</td>
<td>Colored YSZ</td>
<td>0.5 + 1.0 mm</td>
<td>Fully sintered KATANA HT plate (1.0 × 1.0 cm, shade HT13) provided by manufacturer. The veneering ceramic (SBA2, OBA2, A2B, E2 and T1) was fired by an experienced dental technician.</td>
<td>Simulates the occlusal part of a ceramic-veneered YSZ zirconia restoration.</td>
</tr>
<tr>
<td>KATANA ML (Kuraray Noritake)</td>
<td>Colored full-contour YSZ</td>
<td>1.5 mm</td>
<td>Fully sintered KATANA ML plate (1.0 × 1.0 cm) provided by manufacturer.</td>
<td>Simulates the occlusal part of a full-contour zirconia restoration.</td>
</tr>
<tr>
<td>NANOZR (Panasonic)</td>
<td>Ce-TZP/Al₂O₃</td>
<td>0.5 mm</td>
<td>Fully sintered NANOZR plate (1.0 × 1.0 cm) provided by manufacturer.</td>
<td>Simulates the cervical margin of a Ce-TZP/Al₂O₃ zirconia restoration.</td>
</tr>
<tr>
<td>NANOZR + Initial Zr-FS (GC)</td>
<td>Ce-TZP/Al₂O₃</td>
<td>0.5 + 1.0 mm</td>
<td>Fully sintered NANOZR plate (1.0 × 1.0 cm) provided by manufacturer. The veneering ceramic (Frame Modifier, FD91, DA2 CL-F and E) was fired by an experienced dental technician.</td>
<td>Simulates the occlusal part of a Ce-TZP/Al₂O₃ zirconia restoration.</td>
</tr>
<tr>
<td>NANOZR</td>
<td>Ce-TZP/Al₂O₃</td>
<td>1.5 mm</td>
<td>Fully sintered NANOZR plate (1.0 × 1.0 cm) provided by manufacturer.</td>
<td>Simulates the occlusal part of a full-contour zirconia restoration.</td>
</tr>
</tbody>
</table>

Table 2  Overview of the three composite cements and the flowable composite investigated

<table>
<thead>
<tr>
<th>Brand name, lot</th>
<th>Material type</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>Syringe type</th>
</tr>
</thead>
<tbody>
<tr>
<td>G-CEM LinkAce (A2), lot: 1309241</td>
<td>Dual-curing self-etching composite cement</td>
<td>GC; Tokyo Japan</td>
<td>Paste A: Fluoro alumino silicate glass, UDMA, dimethacrylate, silicon dioxide, pigment Paste B: Silicone dimethacrylate, UDMA, dimethacrylate, phosphoric ester monomer, initiator, inhibitor</td>
<td>Automix</td>
</tr>
<tr>
<td>Clearfil Esthetic Cement (Universal), lot: BL0006</td>
<td>Dual-curing self-etching composite cement</td>
<td>Kuraray Noritake; Tokyo, Japan</td>
<td>Paste A: bis-GMA, TEG-DMA, hydrophobic aromatic dimethacrylate monomers, silanated barium glass filler, colloidal silica, accelerator Paste B: bis-GMA, TEG-DMA, hydrophobic aromatic dimethacrylate monomers, hydrophilic aliphatic dimethacrylate monomers, silanated barium glass filler, silanated silica, colloidal silica, benzoyl peroxide, di-camphorquinone, pigments</td>
<td>Automix</td>
</tr>
<tr>
<td>Panavia F 2.0 (Tooth Color), lot: 900031</td>
<td>Dual-curing self-etching composite cement</td>
<td>Kuraray Noritake</td>
<td>Paste A: 10-MDP hydrophobic aromatic and aliphatic photoinitiator, dibenzoyl peroxide dimethacrylate, hydrophilic dimethacrylate, silanized silica Paste B: Hydrophobic aromatic and aliphatic dimethacrylate, sodium aromatic sulphinate, N,N-diethanol-p-toluidine, functionalized sodium fluoride, silanized barium glass</td>
<td>Handmix</td>
</tr>
<tr>
<td>G-aenial Universal Flo (A2), lot: 1303011</td>
<td>Flowable composite</td>
<td>GC</td>
<td>UDMA, bis-MEPP TEG-DMA, silicone dioxide, strontrium glass, pigment, photoinitiator</td>
<td>One-component</td>
</tr>
</tbody>
</table>

Abbreviations: UDMA: urethane dimethacrylate; bis-GMA: 2,2bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl] propane; 10-MDP: 10-methacryloyloxydecyl dimethacrylate; TEG-DMA: triethylene glycol dimethacrylate; bis-MEPP: bisphenol A polyethoxymethacrylate.
Light Transmission and Light Irradiance (LI) Measurement

To monitor LI during light curing, we used a modified light spectrometer disassembled from a MARC patient simulator (BlueLight Analytics; Halifax, Nova Scotia, Canada). The sensor of the light spectrometer was rigidly fixed immediately beneath the slide on which the composite portions were deposited, in order to measure LI directly during light curing. The composite specimens between the microscope slide and coverslip, were immediately placed on the sensor of the light spectrometer to both measure and monitor LI delivered by the two light-curing units mentioned below. The composite specimens were covered with one of the zirconia plates (Table 1), or left uncovered (control), after which they were light cured for 40 s using either G-Light Prima (GC) or SmartLite FOCUS (Dentsply; York, PA, USA) positioned perpendicularly on top and in direct contact with either the zirconia plate or the coverslip. The light spectrometer was sensitive to a LI minimum of 10 mW/cm², which corresponds to 0.4 J/cm². When LI was below the minimum detection sensitivity of the spectrometer, the light energy was considered as 0 J/cm² for further statistical analysis. Per zirconia-composite combination, 5 specimens were prepared and measured (n = 5).

Degree of Conversion (DC) Measurement

After LI measurement and light curing, the specimens were transferred to a micro-Raman spectrometer (SENTERRA, BrukerOptik; Ettingen, Germany). Micro-Raman spectra of each specimen were collected at 5 and 10 min, 1 and 24 h, and at 1 week after light curing using the following settings: 785-nm Ar-ion laser, 100-mW power, 1200 grooves/mm diffraction grating, 50-μm pinhole aperture, and a 100X objective. The spectrum integration time was 20 s, with the recorded spectra averaged over two successive measurements. Each specimen was measured at least twice. All specimens were kept dry and dark at 37°C at all times.

The DC was calculated from the height of the aliphatic C=C peak at 1638 cm⁻¹ and the reference peak according to the following formula:

\[
DC\% = \left(1 - \frac{C_{\text{aliphatic}}}{C_{\text{reference}}} \right) \times 100 (\%)
\]
with $C_{\text{aliphatic}}$ being the absorption peak at 1638 cm$^{-1}$ of the cured specimen, $C_{\text{reference}}$ the reference peak of the cured specimen, $U_{\text{aliphatic}}$ the absorption peak at 1638 cm$^{-1}$ of the uncured specimen, and $U_{\text{reference}}$ the reference peak of the uncured specimen. The reference peak was the C-H peak at 1455 cm$^{-1}$ for G-CEM LinkAce and the aromatic C=C peak at 1608 cm$^{-1}$ for the other two composite cements (Clearfil Esthetic Cement and Panavia F2.0) and the flowable composite (G-aenial Universal Flo). The fraction of remaining C=C double bonds for each spectrum was determined after baseline correction, comparing the maximum heights of the aliphatic and reference peaks using OPUS 7.0 software (BrukerOptik).

A linear mixed-effects model was constructed (R3.0.1 and nlme package, R Foundation for Statistical Computing; Vienna, Austria) to statistically analyze the DC data. In this model, the four fixed effects included were "cement", "zirconia", "curing unit", and log-transformed "time", as well as the mutual interaction "cement" × "zirconia". The individual composite cement specimen was considered as a random effect. All tests were performed at a significance level of $\alpha = 0.05$.

**RESULTS**

**LI Measurement**
The measured LIs are presented graphically for the different experimental groups in Fig 2. The LI of the G-Light Prima light-curing unit was higher than that of the SmartLite FOCUS unit. All zirconia plates clearly decreased LI, irrespective of the curing light employed. The thicker the zirconia plate, the more LI was reduced. A colored YSZ zirconia plate (KATANA HT and KATANA ML, Kuraray Noritake) reduced LI more than a noncolored YSZ zirconia plate (Aadva and Aadva EI). A ceramic-veneered zirconia plate reduced LI more than an equally thick nonveneered zirconia plate. When the Ce-TZP/Al$_2$O$_3$ (NANOZR) zirconia was used, even if only 0.5 mm thick, LI could not be measured; ie, LI was below the detection limit of the MARC patient simulator (10 mW/cm$^2$).

**DC Measurement**
Representative micro-Raman spectra before and after curing of the four composite cements investigated are shown in Fig 3. The measured DCs are graphically presented for
the different experimental groups in Fig 4. The linear mixed-effects model revealed that despite the very different light output, no significant difference in the DC was observed between the two light-curing units for the respective experimental groups (Table 3, p = 0.6858). All other parameters were found to significantly affect the model (Table 3, p < 0.0001).

The DC significantly increased with time for all experimental groups, except for the solely light-cured flowable composite G-aenial Universal Flo when this was cured through the 1.5-mm-thick NANOZR zirconia plates (the non-veneered 1.5-mm-thick Ce-TZP/Al₂O₃ NANOZR plate or the 0.5-mm-thick Ce-TZP/Al₂O₃ NANOZR plate veneered with a 1.0-mm-thick veneering ceramic) by the G-Light Prima light-curing unit, and through the nonveneered 1.5-mm-thick NANOZR zirconia plate by the SmartLite FOCUS light-curing unit. Light curing through the different YSZ zirconia plates did not affect the DC of any of the three composite ce-

Fig 4  Graphs presenting the degree of conversion for the different experimental groups and as measured at the different time points. m: minute, h: hour, w: week.
ments or the flowable composite. The DC of two of the composite cements, namely Clearfil Esthetic Cement and Panavia F2.0, and of the flowable composite, G-aenial Universal Flo, was significantly reduced when light cured through the three different and most opaque Ce-TZP/Al2O3 zirconia (p < 0.0001). In contrast, the DC of the composite cement G-CEM LinkAce was not lower when cured through the Ce-TZP/Al2O3 zirconia. Another exception was that the DC of the composite cement Panavia F2.0 was not significantly reduced at later time points when cured through the Ce-TZP/Al2O3 zirconia, in particular at 24 h and 1 week after light curing. Comparing maximum DCs reached at 1 week after light curing, the DC of Clearfil Esthetic Cement and G-aenial Universal Flo reached over 80%, whereas that of G-CEM LinkAce and Panavia F2.0 were slightly but not significantly lower (range: 70% to 80%). Interestingly, for the three composite cements (G-CEM LinkAce, Panavia F2.0, and Clearfil Esthetic Cement), the difference in LI did not affect the maximum DC in all experimental groups. Only for the flowable composite G-aenial Universal Flo did specimens cured with the interposition of Ce-TZP/Al2O3 zirconia result in significantly lower DC (range: 15% to 60%) than the other groups (approximate range: 75% to 80%).

At 5 min after curing, the DC ranged from 40% to 50% and increased gradually to 70% to 80% one week after curing. For Clearfil Esthetic Cement, most of the specimens showed a relatively high DC (around 60%) at 5 min after curing and reached a DC of 75% to 80% at one week after curing, except for the specimens that were cured through the opaque Ce-TZP/Al2O3 (NANOZR) zirconia. They had significantly lower DCs than the other specimens. The DC of Panavia F2.0 showed a larger variation than that of Clearfil Esthetic Cement and G-aenial Universal Flo. The initial DC of Panavia F2.0 composite cement cured through Ce-TZP/Al2O3 zirconia was very low: around 20% to 30%, but over time, the DC increased to 70% to 75% for all groups. The light-curing flowable composite G-aenial Universal Flo exhibited the least variability, but could not be polymerized properly through Ce-TZP/Al2O3 zirconia.

The DC measured at 5 min after light curing is plotted as a function of the delivered light energy for each specimen in Fig 5. Above the minimum detection sensitivity of the light spectrometer (0.4 J/cm²), none of the composite cements benefitted from additional light energy. Although the G-Light Prima light-curing unit produced higher light energy than did the SmartLite FOCUS unit, the DC was not affected in any experimental group.

**DISCUSSION**

This study investigated the influence of different types of zirconia and their thickness on the LI delivered by light-curing units to the composite cements and the resultant effect on their degree of monomer conversion (DC). Because the interposition of the zirconia plates reduced the delivered light output in all groups, the first null hypothesis should be rejected. Despite the reduced LI, the DC was only temporarily reduced for most groups, and not at all for the composite cement G-CEM LinkAce. Therefore, the second null hypothesis was partially rejected.

The study and specimen setup was designed in close simulation of a clinical luting procedure for zirconia restorations using composite cement. We controlled for the film thickness of the composite cement using 100-μm-thick microscope coverslips to serve as a spacer. Some researchers reported that the cement space of zirconia-based FDPs ranged between 70 and 180 μm; the cement thickness thus standardized in the present study fell within that range. As in the clinical situation the cement would be shielded from exposure to air (except for the margins), the cement portions were covered by glass above and below throughout the whole experiment to prevent polymerization inhibition by oxygen. According to an earlier pilot study, the DC was severely hampered if the mixed cement was exposed to air. Moreover, we observed that the DC of the composite cements stabilized at a lower level when they were not covered with glass, as opposed to the gradual increase in DC measured up to 1 week after light curing in this study. In addition, a practical advantage of micro-Raman spectroscopy over other spectroscopy techniques is that micro-Raman spectra can be acquired through the coverslip.

Three different zirconia grades were selected for the study. The uncolored YSZ Aadvia zirconia can be considered a “conventional” dental zirconia. The YSZ KATANA zirconia was colored and included in the study to investigate the effect of additional zirconia staining. Finally, the Ce-TZP/Al2O3 NANOZR zirconia was included because of its unique and superior physico-mechanical properties, as shown in previous research. For each zirconia grade, three different zirconia plates were prepared to simulate clinical use. The 0.5-mm-thick zirconia plate corresponds more or less to the marginal area of conventional all-ceramic zirconia-based restorations. A 0.5-mm-thick zirconia plate to which a 1.0-mm-thick veneering ceramic was fired corresponds to the occlusal part of conventional all-ceramic zirconia restorations. Finally, a 1.5-mm-thick zirconia plate mimics the occlusal part of conventional all-ceramic zirconia restorations.
clusal part of full-contour zirconia restorations. Since Aadva and KATANA have zirconia options for full-contour application, 1.5-mm-thick Aadva EI and KATANA ML zirconia plates were fabricated (Table 1). Regarding KATANA ML, the zirconia plate was intentionally prepared from the cervical part of the zirconia blank in order to simulate the darkest shade of this grade. In this study, the zirconia surface facing the composite cement did not receive any further surface treatment, although this would have been done in a clinical situation. However, a pilot study showed that additional surface pretreatments, e.g., grinding, sandblasting or polishing, did not affect the LI delivered by the light-curing unit nor ultimately the DC of the composite cement.

The two most common techniques employed to directly measure the DC of composite are Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR FTIR) and micro-Raman spectroscopy. The main advantage of ATR FTIR is that the DC of composite cements can be measured immediately upon mixing. Re-measurements of multiple specimens at later timepoints, as done in this study, is practically rather time consuming; co-monitoring of light transmittance and temperature is also more challenging. The chief advantages of micro-Raman spectroscopy are that specimens can be easily transferred while being shielded from oxygen that may inhibit polymerization, and that light transmittance and
temperature of the specimens can be better controlled. Especially a controlled temperature of 37°C during the experiment is important, since temperature was shown to influence the DC of composite cements considerably. A limitation of micro-Raman spectroscopy is the difficulty in monitoring polymerization behavior during light curing.

Two light-curing units were selected, G-Light Prima and SmartLite FOCUS, which – without zirconia interposition – resulted in significantly different LIs of 2800 and 900 mW/cm², respectively. LI and the light energy delivered by the curing units were assessed using a light spectrometer. This analysis revealed that light was almost unable to penetrate through the Ce-TZP/Al₂O₃ NANOZR zirconia. NANOZR is a ceria-stabilized zirconia, containing 30 vol% Al₂O₃. Because of ceria and Al₂O₃, NANOZR zirconia is more opaque than YSZ zirconia. In this study, two different YSZ zirconia grades were used: Aadva and KATANA. The former YSZ zirconia was left uncolored, whereas the latter YSZ zirconia had a shade (HT13) that corresponds to A2. The zirconia shade affected the transmitted light energy, as was also reported by Ilie et al., who investigated the amount of light passing through zirconia plates of different shades and thicknesses. They reported that colored zirconia significantly reduced the light energy delivered by the light-curing units, and that lightly shaded zirconia thicker than 1.5 mm and more darkly shaded zirconia thicker than 0.5 mm significantly decreased the light energy.

To measure the DC using micro-Raman spectroscopy, the DC is commonly calculated from the decrease in peak intensity of the aliphatic C=C peak at 1638 cm⁻¹ in respect to the stable aromatic C=C reference peak at 1608 cm⁻¹. However, this could not be applied to the composite cement G-CEM LinkAce, which contains urethane dimethacrylate (UDMA) as the main monomer component (Table 2). UDMA does not have a carbon aromatic ring. Nevertheless, two alternative monomer-specific micro-Raman peaks were found for this cement: C=O peak at 600 cm⁻¹ and C-H peak at 1455 cm⁻¹. The flowable composite G-aenial Universal Flo contains both bis-MEPP (bis-phenol A polyethoxymethacrylate) and UDMA (Table 2), by which we could assess the stability of the two alternative reference peaks in comparison to the aromatic C=C peak at 1610 cm⁻¹. We found that the C=O peak at 600 cm⁻¹ continuously decreased upon curing, while the C-H peak at 1455 cm⁻¹ was more stable. We therefore selected the C-H peak at 1455 cm⁻¹ as the reference micro-Raman peak to measure the DC of the composite cement G-CEM LinkAce.

A linear mixed-effects model was applied to statistically analyze the DC data. Such a model, constructed with both fixed and random effects, has been used in several studies before.

For the composite cement G-CEM LinkAce, the delivered light energy did not contribute to the polymerization conversion (DC). Although the light energy delivered to the composite cement G-CEM LinkAce when cured through the NANOZR zirconia was quite low (< 0.4 J/cm²), the polymerization behavior was not different from that observed when the composite cement was cured without the interposition of zirconia. This may mean that the light-curing capacity of this cement is very low, or that the self-curing potential is very high. Within 5 min, the effect of light curing was compensated by the self-curing of the composite cement. This may also have been a reason for the relatively large deviations of DC recorded for the composite cement G-CEM LinkAce.

For Clearfil Esthetic Cement, specimens cured through YSZ zirconia (Aadva and KATANA) revealed a DC that was not different from that of specimens that were cured without interposition of zirconia. However, the specimens that were cured through NANOZR zirconia resulted in a significantly lower DC up to 1 h after light curing. After 24 h, however, this difference in DC between the NANOZR and the other zirconia specimens was negligible. Measurement of LI revealed that the light energy delivered by the light-curing lights was nearly zero or at least below the detection minimum of the light spectrometer (< 0.4 J/cm²). This indicates that the recorded DC of the NANOZR specimens must entirely be ascribed to self-curing.

For the composite cement Panavia F2.0, the recorded DC data showed larger standard deviations than those of the other cements. This is probably related to the hand-mixing of the cement, which can result in a more inhomogeneous distribution of various components and entrapment of air bubbles containing oxygen. The linear mixed-effects model also revealed a slightly lower mean DC as compared to that of Clearfil Esthetic Cement.

In addition, both the self-adhesive composite cement G-CEM LinkAce and the self-etching composite cement Panavia F2.0 contain acidic functional monomers that render the cement more hydrophilic and acidic, as compared to bis-GMA–based composite cements such as Clearfil Esthetic Cement (Table 2). This may also have contributed to the somewhat lower maximum DC obtained for the composite cements G-CEM LinkAce and Panavia F2.0.

For the flowable composite G-aenial Universal Flo, the polymerization trends are slightly different from that of the composite cements, since this material is solely light curing. Therefore, when the specimens did not receive sufficient light energy to cure, eg, when cured through the Ce-TZP/Al₂O₃ zirconia, the DC was significantly lower and did not recover over time. Nevertheless, in the case of the 0.5-mm-thick NANOZR specimens (even when covered by veneering porcelain), some light energy appeared to have been delivered to the specimens, resulting in a partial cure. Solely light-curing flowable composites are contra-indicated for luting restorations based on Ce-TZP/Al₂O₃ zirconia. For all other zirconia, however, enough light could reach the flowable composite to ensure a proper cure, irrespective of the curing light used. As soon as the light spectrometer
was triggered (above 0.4 J/cm²), for all zirconia except NANOZR, the delivered light appeared sufficient to enable the flowable composite to cure properly. Higher light energy, as delivered by the more powerful G-Light Prima light-curing unit, did not alter the curing rate nor improve the maximum DC obtained. This study included a solely light-curing luting protocol, as there is a current clinical trend to lute restorations, in particular those produced with Cerec (Sirona), using solely light-curing composites. Such a light-curing luting protocol is advantageous as it provides the clinician with more time to remove cement excess, which is often clinically difficult, especially in cases of deep cervical and often subgingival margins. In addition, it may enable clinicians to lute restorations using restorative composites on the condition that they possess a sufficiently thin film thickness to not interfere with the restoration’s fit. Such restorative composites are mechanically stronger than composite cements, and are thought to protect the marginal integrity better, being less prone to cement wear and wash-out, especially at stress-bearing occlusal margins.

This study also evaluated whether any correlation existed between the delivered light energy and the DC of the composite cements at 5 min after curing (Fig 5). Unexpectedly, no correlation was found; for all composite cements investigated, the light energy (if above the detection minimum of the light spectrometer; thus not for the Ce-TZP/Al₂O₃ zirconia) did not have any influence on the DC, even at the earliest stage of polymerization. The only effect observed for all dual-curing composite cements, except G-CEM LinkAce, was that when the delivered light energy was undetectably low (< 0.4 J/cm²), the DC was low in the early stage of polymerization, but gradually increased to a level at 1 week that was not significantly different from that obtained without zirconia interposition.

CONCLUSIONS

Based on the results of this in vitro study, the following conclusions regarding the DC of composite cements can be drawn:

1. The zirconia grade and the thickness of the zirconia/veneered zirconia specimen affected the light energy delivered to the composite cement.
2. The type of composite cements did not affect the maximum DC as long as the cements received light.
3. For Ce-TZP/Al₂O₃-based restorations, dual-curing composite cements should be preferred.

ACKNOWLEDGEMENTS

M.I. acknowledges the Flemish scholarship for Japanese students. This work was performed within the framework of the Research Fund of KU Leuven, project 07/10/052, and the Research Foundation Flanders (FWO-Flanders), project G.0431.10.

REFERENCES


Clinical relevance: The new generation of more translucent zirconia may enable the light curing of composite cements through zirconia, thus improving polymerization and luting.