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ORIGINAL ARTICLE

Light- and time-dependent polymerization of dual-cured resin luting agent beneath ceramic

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Abstract

Objective. In this study we investigated the degree of conversion (DC) of a dual-cured resin luting agent beneath a ceramic of different thickness. ***Material and Methods.*** The luting material (RelyX) was photo-activated for 40 s through ceramic disks (Empress Esthetic, 0.7, 1.4, or 2 mm thick). Dual (DUC) and chemically cured (CC) control groups were obtained. A delayed exposure (DE) procedure was tested in which the material was light-activated after 5 min without using ceramic. DC (%) was measured using infrared spectroscopy at 40 s, 1, 2, 4, 6, 8, and 10 min. Light irradiance and spectrum transmitted through ceramic were measured using a power meter and a spectrometer. ***Results.*** A decrease in irradiance was detected with increasing ceramic thickness, but no alteration in the emission profile was observed. At 10 min, all groups showed DC higher than at 40 s. No significant differences were detected for DUC compared with the groups indirectly activated through the ceramic disks. Generally, CC showed the lowest DC values. No significant effect in DC was detected for DE after 10 min. A significant increase in DC was generally detected only up to 4 min. ***Conclusions.*** The luting agent was dependent on light exposure and time to obtain improved DC. Neither the indirect activation nor the DE procedure significantly influenced the final DC.

Key Words: *Degree of conversion, infrared spectroscopy, light-curing, porcelain, resin cement*

Introduction

Ceramic restorations are increasingly attractive in dentistry mainly because of their good esthetics and long-lasting clinical service. Dual-cured resin luting agents are commonly used for ceramic luting purposes. In order to obtain high bond strengths after cementation, it is necessary for adequate light energy to reach the luting material [1]. However, several investigators have reported that ceramics might promote a significant effect of light attenuation, and, as a result, affect the effectiveness of polymerization [2–5]. It is well known that both thickness and shade of the intervening material might reduce light irradiance [2,3,5–8]; a combination of scattering, reflecting, and absorbing properties may explain the reduction in incident light [9].

Nonetheless, little is known about the characteristics of the light irradiated through ceramic, i.e. whether the indirect restorative might affect the quality of the light transmitted. Brodbelt et al. [10] detected that the amount of light directly transmitted through a ceramic is less than 1%, while Watts & Cash [9] observed that the reflected light intensity at the outer surface of the intervening material is appreciable. Moreover, Koch et al. [8] observed that the spectrum profiles for some curing units kept their symmetry after light passage through ceramic, while for other units higher absorbance at lower wavelengths was observed. Therefore, the quality of the light passing through ceramic still warrants investigation.

Previous studies have assessed the hardness of luting materials light-activated through ceramic [2,3,6,7,11], and have usually linked low hardness values to low degree of conversion (DC) values. However, in addition to the conversion of double bonds [4], indirect activation might affect the development of hardness by reducing the light intensity reaching the luting material, hence slowing

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down the polymerization reaction and favoring the formation of less cross-linked polymers [12]. Moreover, in the majority of studies evaluating the polymerization of luting agents under ceramics, thick cement specimens were used, and different results might be found if a clinically relevant thin film were tested.

Furthermore, it has been speculated that a delay in the photo-activation of dual-cured materials would be beneficial in enhancing their DC [13]. The rationale behind this idea is that the immediate exposure to light and formation of cross-linked polymer chains could interfere with the chemical curing by entrapping polymerization promoters and unreacted monomers in the network, therefore interfering with the self-cure mechanism. However, this effect is not yet recognized and warrants investigation.

In order to evaluate whether resin luting agent polymerization would be affected by indirect light activation through different ceramic thicknesses, this study investigated the DC of a dual-cured material beneath ceramic over the course of time. The hypotheses tested were: (1) that the attenuation of light transmitted through the ceramics would reduce the final DC of the luting agent, and (2) that delaying photo-activation exposure would not increase the final DC values.

Material and methods

Ceramic specimens

Ceramic disks 8 mm in diameter made of the leucite-reinforced glass ceramic IPS Empress Esthetic (Ivoclar Vivadent, Schaan, Liechtenstein), shade A3, were obtained in accordance with the manufacturer's instructions. Briefly, three cylindrical patterns were made with organic wax (Thowax, Yeti Dentalprodukte, Engen, Germany), invested with phosphate-based material (Esthetic Speed, Ivoclar Vivadent), and heated at 850°C for 1 h in a ceramic oven (Austromat M, Dekema Dental-Keramiköfen, Freilassing, Germany). The ceramic was then heat pressed into the molds using the EP600 furnace (Ivoclar Vivadent). Afterwards, the specimens were wet-polished with 400-, 600-, and 1200-grit SiC carbide papers to thicknesses of 0.7, 1.4, and 2 mm.

Light characteristics

The quartz-tungsten-halogen light-curing unit XL3000 (3M ESPE, St. Paul, Minn., USA) was connected to a voltage stabilizer and the irradiance level was checked with a digital power meter (Ophir Optronics, Danvers, Mass., USA). The irradiance value transmitted through each ceramic disk was also obtained. One measurement was carried out for each condition. Furthermore, the spectral distribution of the light transmitted through each ceramic specimen was obtained using a computer-controlled spectrometer (USB2000, Ocean Optics, Dunedin, Fl., USA) and compared with the control profile (without the intervening material).

Degree of conversion as a function of time

The real-time DC of the dual-cured resin luting material RelyX ARC (3M ESPE, shade A3) was evaluated using Fourier transform infrared spectroscopy (Prestige21, Shimadzu, Columbia, MD, USA), with an attenuated total reflectance device composed of a horizontal ZnSe crystal. Equal volumes of base and catalyst pastes of the luting agent were mixed for 15 s, placed on the crystal and covered with a transparent polyester strip. The ceramic disks were positioned over the polyester strip and photo-activated for 40 s, with the light guide tip placed in contact with the disk, defining the following groups: 0.7 mm ceramic (C − 0.7), 1.4 mm ceramic (C − 1.4), and 2 mm ceramic (C − 2). Figure 1 is a schematic illustration of the test set-up. The dual-cured control group (DUC) was defined by direct activation without using ceramic. The chemically cured control group (CC) was obtained by shielding the material from the curing light. In addition, a group was obtained in which the exposure to photo-activation was conducted 5 min after the mixing procedure (delayed exposure – DE), without using ceramic.

After photo-activation, the material was shielded from the ambient light. After 40 s (end of activation

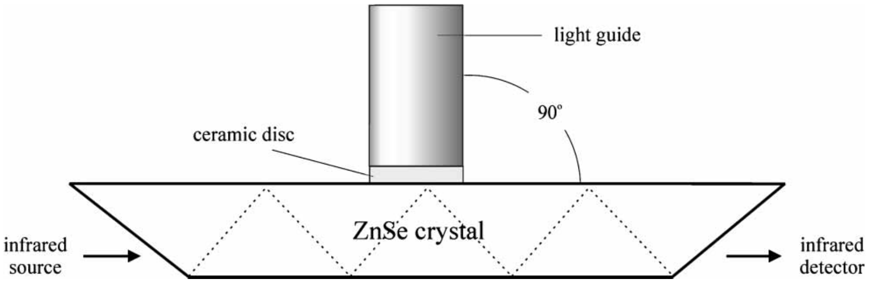

Figure 1. Schematic illustration of the infrared spectroscopy set-up. After mixing the base and catalyst pastes, the luting agent was placed on the crystal and covered with a transparent polyester strip. The ceramic disks were positioned over the polyester strip and photo-activated for 40 s with the light guide tip placed in contact with the disk.

time), 1, 2, 4, 6, 8, and 10 min, the DC (%) of the luting material was evaluated using a baseline technique [14]. Twelve scans were taken, with a resolution of 4 cm^{-1}, considering the intensity of C = C stretching vibration (peak height) at 1635 cm^{-1} and as an internal standard, using the symmetric ring stretching at 1608 cm^{-1}, from both polymerized and unpolymerized samples. DC was determined by subtracting the percentage of remaining aliphatic C = C from 100%. The analyses were carried out in triplicate, and data analyzed by two-way repeated measures ANOVA (activation mode vs time) and Tukey's test ($p < 0.05$), using the SigmaStat 3.11 software (Systat Software Inc., San Jose, Calif., USA).

Results

Light characteristics

The irradiance level of the light-curing unit was 605 mW/cm^2. A decrease in light irradiance was detected with increasing ceramic thickness: 486 mW/cm^2 (0.7 mm), 390 mW/cm^2 (1.4 mm), and 258 mW/cm^2 (2 mm). Figure 2 displays the light spectrum profiles emitted through the different ceramic specimens. Compared with the control profile, no significant alteration for any ceramic disk was observed; the wavelength range of emission (400–510 nm) and the peak position on the curve (484 nm) were the same for all groups.

Degree of conversion as a function of time

Table I presents the results for the time-dependent conversion of all groups. The factors "activation mode" and "time" were significant, as was their interaction ($p < 0.001$). At 40 s, all except the CC and DE groups showed a DC higher than 66%. At 10 min, the DC for all groups was significantly higher than at 40 s ($p < 0.001$). Also, at 10 min, CC showed significantly lower DC than all the remaining groups ($p < 0.001$), which presented similar results ($p \geq 0.431$). No significant differences were detected for DUC compared with C-0.7, C-1.4, and C-2, regardless of the time ($p \geq 0.431$).

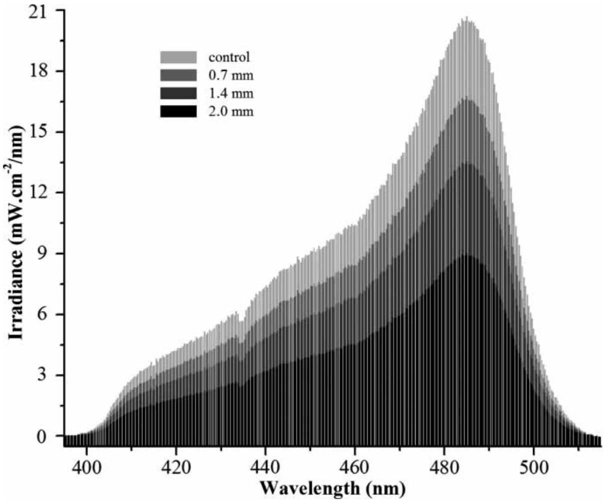

Figure 2. Light spectrum profiles emitted through the different ceramic disks. No significant alteration was observed in the emission profile for activation through ceramic when compared with the control profile, and regardless of the ceramic thickness. The wavelength range of emission (400–510 nm) and the peak position on the curve (484 nm) were the same for all groups.

Irrespective of the time, CC showed significantly lower DC than all other groups ($p < 0.001$), except for DE, which showed significantly higher DC than CC starting from 6 min ($p < 0.001$). In addition, no significant effect was detected for delaying the light exposure: despite the lower initial values for DE, this group showed similar DC to all photo-activated groups after 6 min ($p \geq 0.663$). In general, when observing the DC over the course of time, a significant increase was detected only up to 4 min. For CC, a significant increase in DC was observed for each time compared with the previous one ($p < 0.001$), except for 40 s and 1 min ($p = 0.341$).

Discussion

The first hypothesis tested was rejected, as indirect activation did not reduce the DC of the dual-cured luting material. The conversion of double bonds by photo-activation is reliant on a minimum energy dose being delivered to excite the photo-initiator and produce a sufficient number of free radicals for polymerization. Although different irradiance levels were transmitted through the different ceramic disks, the results of this study suggest that these light energy differences were not great enough to yield significant differences in DC, irrespective of the time. This outcome does not corroborate those of other studies that observed lower hardness or DC values for increased ceramic thickness [4,6,11].

There are two potential explanations for the differences in findings between the present investigation and previous studies: (1) a thin, clinically relevant luting agent film was tested in the present study, while in other studies hardness and DC are usually measured in thick cement specimens, with reduced light penetration within the bulk of the material; (2) despite the good relationship previously described between hardness and DC [15], other features that might interfere with the hardness result include the chemical structure of the monomers involved and the type and density of network cross-linking [16].

When observing the conversion over the course of time, a continuous increase was detected. At 10 min, the DC was significantly higher than at 40 s for all groups. This finding indicates that chemical curing is effective in increasing the DC even when immediate photo-activation is performed. In addition, the present study evaluated the effect of delaying the

Table I. Means (SD) for degree of conversion (%) over the course of time.

	Time						
Group	40 s	1 min	2 min	4 min	6 min	8 min	10 min
Dual control (DUC)	69.5 (0.9)^{C,a}	74.5 (5.0)^{BC,a}	76.5 (3.2)^{B,a}	77.3 (3.2)^{AB,a}	78.8 (2.7)^{AB,a}	80.1 (3.3)^{AB,a}	82.1 (4.3)^{A,a}
0.7 mm ceramic (C-0.7)	66.8 (7.7)^{C,a}	72.3 (2.8)^{B,a}	75.3 (2.0)^{AB,a}	75.8 (2.0)^{AB,a}	77.1 (1.6)^{AB,a}	79.4 (3.2)^{A,a}	80.6 (3.9)^{A,a}
1.4 mm ceramic (C-1.4)	68.1 (4.4)^{C,a}	71.1 (1.9)^{BC,a}	72.2 (1.0)^{ABC,a}	73.8 (2.2)^{AB,a}	74.7 (1.8)^{AB,a}	76.1 (0.7)^{AB,a}	76.6 (0.8)^{A,a}
2 mm ceramic (C-2)	69.7 (3.2)^{B,a}	70.1 (4.2)^{B,a}	71.3 (3.5)^{B,a}	73.8 (1.0)^{AB,a}	77.0 (2.3)^{A,a}	77.0 (1.2)^{A,a}	78.9 (1.2)^{A,a}
Delayed exposure (DE)	8.3 (7.1)^{D,b}	10.6 (5.7)^{CD,b}	15.3 (6.0)^{C,b}	37.2 (4.4)^{B,b}	74.5 (2.4)^{A,a}	76.7 (2.6)^{A,a}	77.9 (3.4)^{A,a}
Chemical control (CC)	7.9 (3.2)^{E,b}	11.3 (5.8)^{E,b}	17.5 (4.1)^{D,b}	37.1 (2.6)^{C,b}	49.9 (3.2)^{B,b}	57.8 (3.8)^{A,b}	61.1 (2.4)^{A,b}

Means followed by distinct capital letters in the same line, and small letters in the same column, are significantly different at $p < 0.05$.

photo-activation procedure, and it seems that it might not be beneficial for increasing the final DC of dual-cured agents. Therefore, the second hypothesis was confirmed. On the other hand, it is known that the polymerization rate (R_p) for self-polymerization is lower than it is for light-polymerization [17], and also that high R_p values are related to increased shrinkage stress development [18]. Therefore, the DE procedure might be beneficial in reducing the shrinkage stress of dual-cured luting materials, as the R_p is probably lower, although this effect needs further investigation in order to be confirmed. Nevertheless, it is not known whether the DE procedure could interfere with the physical properties of the polymer, and this issue also warrants investigation.

In addition to the attenuation effect, it could be speculated that the intervening material could alter the light spectrum of wavelengths transmitted through it. Koch et al. [8] described how the spectrum profiles for some curing units kept their symmetry after transmission through ceramic, while for other units a higher absorbance at lower wavelengths was observed. The recently introduced leucite-reinforced glass ceramic used in this study, Empress Esthetic, presents increased translucency, smaller grain size, and leucite crystals distributed in a more homogeneous manner than in its predecessor, Empress. Although little is known about the transmittance characteristics of these two materials, the present results indicate that Empress Esthetic, irrespective of its thickness, allowed irradiance transmission without interfering in the wave properties of the light.

The results of the present study have clinical implications; although chemical curing might compensate for the lower irradiance that reaches the dual-cured luting material, the photo-activation procedure is essential for obtaining improved DC. Therefore, the use of curing units with sufficient irradiance to compensate for light attenuation by the ceramic is advisable to achieve a sufficiently high DC. However, the results of the present study do not take into account other effects that might interfere with the activation of luting agents under ceramics, such as different irradiance levels of curing devices or different shades and opacities of the intervening restorative. Further studies are therefore necessary.

In conclusion, the dual-cured luting agent was dependent on light exposure and time to obtain improved DC. Indirect activation through ceramic showed no significant detrimental effect on the DC, and the DE procedure showed no significant beneficial effect of increasing the conversion of the dual-cured material.

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