Effect of Insufficient Light Exposure on Polymerization Kinetics of Conventional and Self-adhesive Dual-cure Resin Cements

Y Jang • JL Ferracane • CS Pfeifer • JW Park • Y Shin • BD Roh

Clinical Relevance

Insufficient light exposure could result in low degree of conversion of dual-cure resin cement, which is even lower than that of self-curing alone. Clinicians need to modify their curing strategies when sufficient light activation is difficult to achieve.

SUMMARY

Objectives: The purpose of this study was to investigate the influence of insufficient light

Youngjune Jang, DDS, PhD, Yonsei University, Department of Conservative Dentistry and Oral Science Research Center, College of Dentistry, Seoul, Republic of Korea

Jack L Ferracane, PhD, Oregon Health & Science University, Restorative Dentistry, Portland, OR, USA

Carmem Silvia Pfeifer, DDS, PhD, Oregon Health & Science University, Restorative Dentistry, Portland, OR, USA

Jeong-Won Park, DDS, MSD, PhD, Yonsei University, Department of Conservative Dentistry and Oral Science Research Center, College of Dentistry, Gangnam Severance Hospital, Seoul, Republic of Korea

Yooseok Shin, DDS, MSD, PhD, Yonsei University, Department of Conservative Dentistry and Oral Science Research Center, College of Dentistry, Seoul, Republic of Korea

*Byoung-Duck Roh, DDS, MSD, PhD, Yonsei University, Department of Conservative Dentistry and Oral Science Research Center, College of Dentistry, Seoul, Republic of Korea

*Corresponding author: 50-1 Yonsei-ro, Seodaemun-gu, Seoul 03722, Republic of Korea; e-mail: operatys16@yuhs. ac

DOI: 10.2341/15-278-L

exposure on the polymerization of conventional and self-adhesive dual-cure resin cements under ceramic restorations.

Methods: Two conventional dual-cure resin cements (Rely-X ARC, Duolink) and two self-adhesive resin cements (Rely-X U200, Maxcem Elite) were polymerized under different curing modes (dual-cure or self-cure), curing times (20 and 120 seconds), and thickness of a ceramic overlay (2 and 4 mm). Polymerization kinetics was measured by Fourier transform infrared spectroscopy for the initial 10 minutes and after 24 hours. Data were analyzed using mixed model analysis of variance (ANOVA), one-way ANOVA/Student-Newman-Keuls post hoc test, and paired t-test (α =0.05).

Results: When light-curing time was set to 20 seconds, the presence of the ceramic block significantly affected the degree of conversion (DC) of all resin cements. Especially, the DC of the groups with 20 seconds of light-curing time under 4 mm of ceramic thickness was even lower than that of the self-cured groups at 24 hours after polymerization (p<0.05). However, when light-curing time was set to 120 seconds,

E2 Operative Dentistry

a similar DC compared with the group with direct light exposure (p>0.05) was achieved in all dual-cure groups except Maxcem Elite, at 24 hours after polymerization.

Conclusions: For both conventional and selfadhesive dual-cure resin cements, insufficient light exposure (20 seconds of light-curing time) through thick ceramic restoration (4 mm thick) resulted in a DC even lower than that of self-curing alone.

INTRODUCTION

Nowadays, dual-cure resin cements have been the material of choice in bonding of ceramic restorations. They rely both on light-cure and chemical-cure mechanisms in an attempt to ensure sufficient polymerization throughout the material, even without proper light activation. However, it has been claimed that the two components do not always work synergistically. 1-3 Meng and others 4 reported poor microhardness of dual-cured resin cements, even lower than the self-cured group, when it was insufficiently light-activated through a 3-mm-thick ceramic restoration overlay. They suggested that the early vitrification induced by insufficient light activation could interfere with the subsequent selfpolymerization, compromising the overall polymerization of dual-cure resin cements.

This is an important issue when considering that predictable outcomes of ceramic restorations are closely associated with sufficient polymerization of underlying resin cement.⁵ However, there has been a lack of evidence regarding the characteristics of this phenomenon. It is essential to observe the initial polymerization kinetics to understand the polymerization characteristics of materials in different conditions; however, few studies have provided such information having only presented intermittent measurements such as microhardness at 24 hours after polymerization.4 Therefore, the understanding of this issue remains unclear, and accordingly, the risk of insufficient light exposure on dual-cure resin cement has not been well recognized in the field of restorative dentistry. Most manufacturers do not consider ceramic thickness when recommending light-curing protocols for dual-cure resin cements, which is one of the major factors that determines the amount of light transmission.^{6,7} Moreover, several manufacturers have recommended even further reduced light-curing times, ie, 20 seconds or below, for some recent materials. Therefore, there is a need to verify this issue and make guidelines that are clinically relevant.

The purpose of this study was to investigate the influence of insufficient light exposure on the polymerization of conventional and self-adhesive dual-cure resin cements under ceramic restorations. For this, several different light-curing conditions were simulated by combining the ceramic restoration thicknesses and the light-curing times, and polymerization kinetics were measured for the initial 10 minutes and then followed up after 24 hours. The null hypothesis tested was as follows: dual-cured resin cements always show higher degree of conversion (DC) compared to self-cured resin cements.

METHODS AND MATERIALS

Fabrication of Ceramic Blocks

Lithium disilicate ceramic blocks (10×10 mm, IPS e.max CAD/CAM, shade A3, low translucency, Ivoclar Vivadent, Schaan, Liechtenstein) were cut by low-speed diamond saw (Dk-2610, Struers Minitom, Rodovre, Denmark) and polished with 400-, 600-, and 800-grit silicon carbide papers, and their final thickness was adjusted to 2.00 ± 0.01 and 4.00 ± 0.01 mm. They were cleaned with ultrasonic cleaner (BioSonic UC50D, Coltène/Whaledent, Cuyahoga Falls, OH, USA) for 5 minutes and then subjected to the crystallization process in a ceramic furnace (Programat P300, P81 mode, Ivoclar Vivadent).

Experimental Groups

Two conventional dual-cure resin cements and two self-adhesive resin cements were studied (Table 1). Each group of resin cement contained six subgroups (2 ceramic thicknesses \times 2 different light-curing times + 1 positive control (direct light exposure [DLE]) + 1 negative control (self-cured [SC]). Five specimens were prepared for each subgroup (n=5). The descriptions of the tested groups are given in Table 2.

Measurement of the Curing Light Intensity Through Ceramic Blocks

The light transmission value of an LED curing light (Bluephase, Ivoclar Vivadent) was measured with a laser power meter (Powermax 5200, Molectron, Portland, OR, USA) with and without a ceramic block. Measurements were repeated five times for each group, and the average value was calculated (Table 3).

Specimen Preparation

Resin cements were mixed according to the manufacturer's instructions and placed on a glass slide.

Table 1: Dual-cure Resin Cements and Self-Adhesive Resin Cements Used in This Study								
Resin cement	nt Manufacturer Shade Recommended light exposure protocol		Batch					
Rely-X ARC	3M ESPE, St Paul, MN, USA	Transparent	Light cure 40 s/surface	N352609				
Duolink	Bisco, Schaumburg, IL, USA	Transparent	Light cure 40 s/surface	1200003240				
Rely-X U200 (Self adhesive)	3M ESPE, St Paul, MN, USA	Transparent	Single surface, from occlusal: 20 seconds	491292				
			Any other surface: additional 20 seconds					
Maxcem Elite (Self adhesive)	Kerr, Orange, CA, USA	Clear	Light cure 10 seconds when irradiance is 1000 mW/cm ²	4720553				
			Light cure 20 seconds when irradiance is 600 mW/cm ²	_				

Adhesive tape (Scotch Tape, 3M, St. Paul, MN, USA) was applied to the glass slide before resin cement placement and served as a spacer ($100\pm10~\mu m$) to ensure a constant thickness of the resin cement layer. Then resin cement was covered with a Mylar strip and pressed with another slide glass to remove the excess cement. Then a ceramic block (2 or 4 mm thick) was placed above the Mylar strip. For the SC group, a 2-mm-thick ceramic block was placed on the specimen. For the DLE group, additional glass slides were placed over the specimen to control the distance between the light-curing unit tip and the specimen at 2 mm (Figure 1).

Measurement of Degree of Conversion

The specimen was mounted in a plastic holder and placed in the Fourier transform infrared spectrometer (Nicolet 6700 FT-IR Spectrometer, Thermo, Madison, WI, USA) at a 45° vertical angle (Figure 1). Infrared spectra were recorded immediately after the placement, and then the specimen was illuminated with the LED curing light for 20 or 120 seconds, except for the SC group. During the illumination, the curing light was fixed with an additional holder to maintain a uniform position throughout the whole experiment. Spectra collection was set up between 6140 and 6200 cm⁻¹ on transmission enhanced synchronous protocol, near infrared (IR) mode, taking one spectrum per second

Table 2: Experimental Groups With Different Ceramic Thickness and Curing Methods Ceramic Curing Resin cements and code thickness. of experimental groups time, s mm Rely-X **Duolink** Rely-X Maxcem ARC U200 Elite D DLE U DLE M DLE 0 120 A DLE 2 120 A 2-120 D 2-120 U 2-120 M 2-120 2 20 A 2-20 D 2-20 U 2-20 M 2-20 U 4-120 4 120 A 4-120 D 4-120 M 4-120 A 4-20 D 4-20 U 4-20 M 4-20 4 20 2 0 A SC D SC U SC M SC

(2 scans/spectrum) at 4 cm⁻¹ resolution. Data collection was continued for 600 seconds, and each test condition was replicated five times. DC was calculated by the following equation:

$$DC(\%) = \{1 - (Peak \ area \, [p]/Peak \ area \, [u])\} \times 100(\%),$$

where u and p refer to the unpolymerized and polymerized cement, respectively, with the reaction peak set at 6165 cm⁻¹. Peak area (u) was calculated by averaging values over the first 20 seconds before light exposure (40 data points), and peak area (p) was measured twice at 10 minutes and 24 hours after data collection. Peak area (p) at 10 minutes was calculated by averaging values of the last 50 seconds (100 data points), and peak area (p) at 24 hours was calculated by averaging values for 20 seconds (40 data points) after 24 hours.

The polymerization rate curve was obtained by taking the first derivative of the DC regarding the time. The maximum value of the derivative was taken as the maximum polymerization rate (Rp max, $\Delta DC\%/s$), and the time required to reach the Rp max was taken as the time of maximum polymerization rate (Time of Rp max, seconds).

Polymerized specimens were removed from the holder after 10 minutes, and resin cement thickness was measured with a digital micrometer (Absolute Digimatic Caliper, Mitutoyo Corp, Aurora, IL, USA)

Table 3: Light Transmittance Mean Values (SD) for Each Experimental Condition (n=5) Positive Experimental control group groups Ceramic thickness, 0 2 4 Distance from 2 2 4 light-curing unit, mm Irradiance, 1085.4 (6.3)a 128.2 (2.6)b 25.6 (0.9)° mW/cm²

Significant differences are shown by different letters within row according to Student-Newman-Keuls post hoc test (p<0.05).

E4 Operative Dentistry

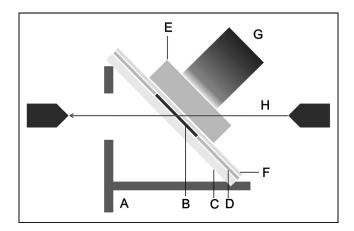


Figure 1. Specimen positioning. (A) Holder; (B) resin cement; (C) slide glass; (D) adhesive tape; (E) ceramic block or slide glass; (F) mylar strip; (G) light-curing unit tip; and (H) IR path.

to ensure uniform thickness among the specimens. Then both dual-cured and self-cured specimens were stored in light-proof, dry conditions at 25°C for 24 hours. An IR spectrum was collected again for each specimen after 24 hours, and the DC was calculated.

IR spectra data were extracted from the IR spectra analysis software package OMNIC 6.0 (Thermo Electron, Inc, Madison, WI, USA). Raw data were analyzed by PeakFit v4.12 (Systat Software, Inc, San

Jose, CA, USA) and smoothed under the Loess algorithm, 2.0% level. A representative curve was obtained by averaging data of five specimens in each group.

Statistical Analysis

Statistical analysis was performed using SPSS version 20 (SPSS Inc, Chicago, IL, USA). For DC of resin cements, one-way analysis of variance (ANOVA) was done between six groups (4 experimental groups + 2 control groups) to compare DC (%) at 10 minutes, DC (%) at 24 hours, Rp max (Δ DC %/s), and time of Rp max (seconds), and a Student-Newman-Keuls post hoc test was done for multiple comparisons. Then the paired t-test was done to compare DC (%) at 10 minutes and DC (%) at 24 hours for each group. For light transmission values of curing light, one-way ANOVA was done, followed with a Student-Newman-Keuls post hoc test for multiple comparisons (α =0.05).

RESULTS

Table 4 shows the mean and standard deviations (SD) of the DC (%), Rp max (Δ DC %/s), and time of Rp max (seconds) of the four resin cements. Light transmittance values for each experimental condition are given in Table 3.

Table 4: DC (%) (SD) at 10 Minutes and 24 Hours After Polymerization, Maximum Polymerization Rate (△DC %/s), and Time of Maximum Polymerization Rate (Seconds) of Rely-X ARC, Duolink, Rely-X U200, and Maxcem Elite

Rely-X ARC	A DLE	A 2-120	A 4-120	A 2-20	A 4-20	A SC
DC 10 minutes	80.65 (0.69) ^{A,b}	78.89 (1.10) ^{B,b}	75.09 (2.07) ^{C,b}	71.92 (1.02) ^{D,b}	63.46 (1.71) ^{E,b}	56.25 (0.86) ^{F,b}
DC 24 hours	86.97 (0.97) ^{A,a}	86.48 (0.97) ^{A,a}	85.29 (2.27) ^{A,a}	82.82 (0.94) ^{B,a}	75.78 (2.22) ^{D,a}	78.98 (1.68) ^{C,a}
Rp max	7.42 (0.82) ^A	4.80 (0.40) ^B	3.44 (0.60) ^C	4.73 (0.38) ^B	2.75 (0.41) ^D	1.08 (0.18) ^E
Time of Rp max	4.55 (0.73) ^B	7.33 (1.23) ^B	13.07 (1.97) ^B	8.42 (0.93) ^B	10.69 (2.23) ^B	137.38 (33.14) ^A
Duolink	D DLE	D 2-120	D 4-120	D 2-20	D 4-20	D SC
DC 10 minutes	69.27 (1.66) ^{A,b}	69.62 (1.44) ^{A,b}	69.69 (1.20) ^{A,b}	62.95 (1.30) ^{B,b}	60.23 (1.13) ^{C,b}	53.79 (1.30) ^{D,b}
DC 24 hours	74.55 (1.84) ^{A,a}	74.74 (1.24) ^{A,a}	75.56 (0.51) ^{A,a}	69.65 (1.45) ^{B,C,a}	68.05 (1.10) ^{C,a}	70.91 (1.23) ^{B,a}
Rp max	7.51 (1.22) ^A	3.98 (0.61) ^B	2.47 (0.22) ^C	4.17 (0.36) ^B	2.52 (0.27) ^C	0.65 (0.13) ^D
Time of Rp max	3.07 (0.65) ^B	4.55 (0.89) ^B	9.90 (1.26) ^B	4.36 (0.73) ^B	12.87 (0.78) ^B	144.10 (42.04) ^A
Rely-X U200	U DLE	U 2-120	U 4-120	U 2-20	U 4-20	U SC
DC 10 minutes	65.38 (1.21) ^{A,b}	65.47 (1.70) ^{A,b}	63.75 (1.27) ^{A,b}	56.92 (1.53) ^{B,b}	49.39 (2.44) ^{C,b}	30.63 (2.81) ^{D,b}
DC 24 hours	71.63 (1.28) ^{A,a}	71.86 (1.88) ^{A,a}	69.78 (0.65) ^{A,a}	64.28 (1.60) ^{B,a}	58.14 (1.69) ^{D,a}	61.73 (2.17) ^{C,a}
Rp max	5.04 (0.90) ^A	2.80 (0.29) ^B	2.59 (0.45) ^B	3.00 (0.36) ^B	2.32 (0.55) ^B	0.61 (0.27) ^C
Time of Rp max	4.55 (0.73) ^B	4.85 (0.41) ^B	9.60 (1.90) ^B	4.65 (0.75) ^B	7.03 (2.85) ^B	170.68 (45.15) ^A
Maxcem Elite	M DLE	M 2-120	M 4-120	M 2-20	M 4-20	M SC
DC 10 minutes	69.97 (2.03) ^{A,b}	68.31 (1.41) ^{A,b}	63.39 (2.96) ^{B,b}	55.84 (1.25) ^{C,b}	48.43 (3.11) ^{D,b}	54.77 (1.21) ^{C,b}
DC 24 hours	75.48 (2.18) ^{A,a}	74.56 (1.69) ^{A,a}	70.80 (3.49) ^{B,a}	64.57 (1.07) ^{C,a}	59.50 (2.33) ^{D,a}	69.61 (1.14) ^{B,a}
Rp max	3.22 (0.72) ^A	1.78 (0.36) ^B	1.88 (0.29) ^B	1.58 (0.23) ^B	1.67 (0.19) ^B	0.96 (0.10) ^C
Time of Rp max	4.36 (1.07) ^B	7.33 (1.54) ^B	10.89 (1.64) ^B	7.72 (1.34) ^B	10.79 (1.33) ^B	94.50 (14.83) ^A
0' '" ' ""	111 1 1166					" . 0: 1 .

Significant differences are written by different letters (uppercase letters within row; lowercase letters within column) within each resin cement according to Student-Newman-Keuls post hoc test (p<0.05).

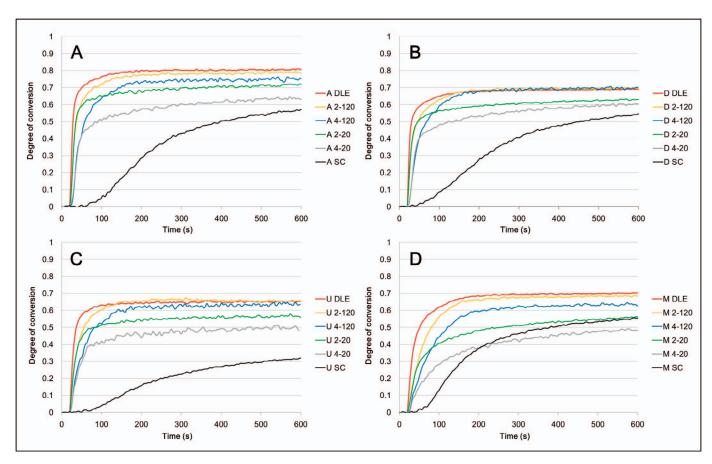


Figure 2. Representative real-time polymerization profiles of (A) Rely-X ARC, (B) Duolink, (C) Rely-X U200, and (D) Maxcem Elite according to light-curing condition during the initial 10 minutes.

Polymerization Kinetics (0-10 Minutes)

Figure 2 shows the effects of light-curing condition on the real-time polymerization profile for each resin cement. Generally, the dual-cure groups showed a rapid DC increase immediately after the light exposure, whereas the self-cure groups showed a more gradual increase. Figure 3 describes polymerization rate as a function of DC. When assuming the point of DC with Rp max as the vitrification point, 11 dual-cure groups with a 4-mm-thick ceramic overlay revealed early vitrification in relation to other dualcure groups, whereas the point of vitrification was not apparent in self-cure groups (Figure 3). The overlying ceramic thickness (0, 2, and 4 mm thick) significantly influenced Rp max and time of Rp max (Table 4), which is directly related to the polymerization profile before 20 seconds.

DC (10 Minutes and 24 Hours)

At 10 minutes after polymerization, significantly higher DC was observed in all dual-cure groups compared with the self-cure group, except Maxcem Elite. However, at 24 hours after polymerization, the DC of the self-cure groups equaled or surpassed that of the 4-mm, 20-second groups regardless of the material, and the M SC group showed even higher DC compared with M 2-20 and M 4-20 groups (p<0.05), which means there was even more increase of DC in the self-cure group (Table 4; Figure 4)

The self-cured group revealed the highest DC increase for all resin cements when comparing 10 minutes and 24 hours (Table 4). For the dual-cured groups, the DC increase had a trend of inverse relationship with the amount of initial light energy received.

When light-curing time was set to 20 seconds, DC was significantly affected by the presence of the ceramic block, resulting in significantly lower values compared with the group with DLE at 24 hours after polymerization (p<0.05). However, when light-curing time was set to 120 seconds, a similar DC compared with the group with DLE (p>0.05) was achieved in all dual-cure groups at 24 hours,

E6 Operative Dentistry

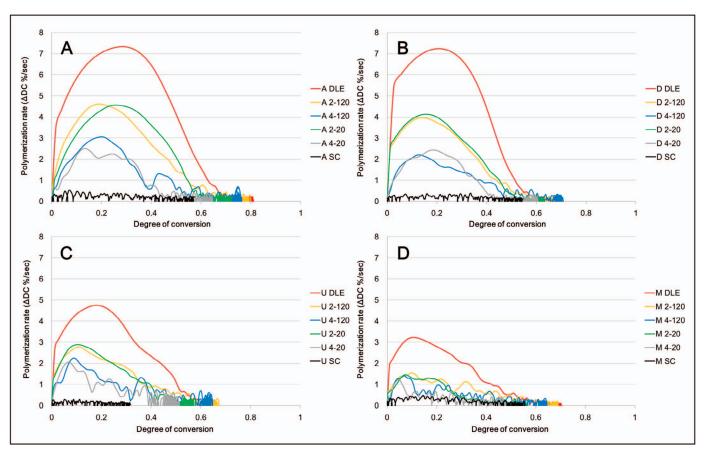


Figure 3. Polymerization rate as a function of DC for (A) Rely-X ARC, (B) Duolink, (C) Rely-X U200, and (D) Maxcem Elite according to light-curing condition during the initial 10 minutes.

regardless of the ceramic thickness, except Maxcem Elite at 4 mm (Table 4; Figure 4).

DISCUSSION

The most notable point of this study is that all 4-mm, 20-second groups showed significantly lower DC compared with the SC groups at 24 hours after polymerization, rejecting the null hypothesis (Table 4; Figure 4). This confirms that insufficient light exposure of a self-adhesive resin cement could result in incomplete polymerization, even lower than that of self-curing alone, which is consistent with previous studies that investigated conventional dual-cure resin cements.^{2,4}

As dimethacrylate-based dental composites are polymerized, mobility of radicals becomes restricted by the growing cross-linked polymer network, and radicals become essentially immobilized after the point of vitrification.² In the dual-cure mode, light activation induces rapid polymerization, with large amounts of free radicals becoming trapped within the organic matrix at the initial stage of polymeri-

zation, if insufficient curing energy is applied to drive the reaction further to completion. 1-3 Considering that the self-cure mechanism proceeds more slowly, the early vitrification brought on by the initial light activation minimizes the extent of the subsequent self-polymerization of the dual-cure resin cement, due to restricted molecular mobility. When a sufficient amount of light energy is delivered to a dual-cure resin cement, this kind of competitive reaction would not be apparent because the dualcure resin cement has been polymerized well even if the self-cure component becomes partially impaired. In contrast, in the absence of light energy being delivered to the resin cement, a certain degree of polymerization could be attained solely due to the progress of the self-cure component. In this study, dual-cure groups with insufficient light exposures (4mm, 20-second and 4-mm, 120-second groups) revealed early vitrification in relation to other dual-cure groups (Figure 3), which is known to be associated with the reduction in overall amount of polymerization. 11 Meanwhile, the point of vitrification was not apparent in self-cure groups (Figure 3),

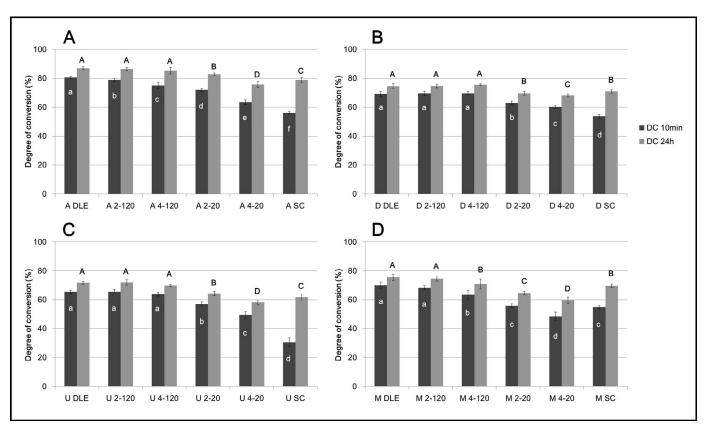


Figure 4. DC (%) (SD) of Rely-X ARC, Duolink, Rely-X U200, and Maxcem Elite at 10 minutes and 24 hours after polymerization. Significant differences are written by different letters (uppercase letters for DC at 24 hours after polymerization; lowercase letters for DC at 10 minutes after polymerization) according to Student-Newman-Keuls post hoc test (p<0.05).

which could be associated with more molecular mobility and large amounts of delayed polymerization as a consequence. Therefore, cases in which insufficient energy could be applied to the cement, it would be better, from the standpoint of DC, to allow the self-cure reaction to progress without additional light exposure.

When considering that the total light energy applied for the DLE group (130,248 mJ/cm²) was about 40 times higher compared with the 4-mm, 120second group (3072 mJ/cm²) in this study, the similar DC of both groups cannot be explained based on the light energy-based polymerization concept. However, recent studies suggest that DC is not directly proportional to the total amount of energy applied to resin cement. 13-15 It should be noted that the light energy (mJ/cm²) reveals simply the number of photons per unit area, and delivering more photons does not necessarily result in more activated photo-initiators and free radicals, because of rapid saturation of the photo-initiator system and restricted availability of monomers. Therefore, the large discrepancy of received light energy between the two groups cannot be the key factor explaining the polymerization of the 4-mm, 120-second group. Musanje and others¹⁵ reported that when sufficiently long light-curing time is provided, adequate polymerization can be achieved even at very low light irradiance (25 mW/cm²). Although "sufficiently long" light-curing time would vary depending on the composition of the resin cement, 120 seconds of light-curing time was effective in three of the four resin cements tested in this study. Therefore, prolonged light-curing time could be an option to improve the polymerization level of dual-cure resin cement.

Rely-X U200 showed low DC in self-cure mode at 10 minutes after mixing, being less than half of that of U DLE group. However, it should be noted that the DC recovered to a level similar to that of U 2-20 (p>0.05) at 24 hours after polymerization, showing a large amount of delayed polymerization (Table 4; Figure 4). Such low initial polymerization rate and large delayed polymerization are general features of self-adhesive resin cements, and others have pointed out the presence of acidic functional monomers in the self-adhesive resin cements as the major cause. 16,17 Acidic functional monomers are believed to deactivate free radicals of methacrylate and

E8 Operative Dentistry

produce an acid-base setting reaction, inducing a low rate of co-polymerization and increased delayed polymerization.¹⁷ As shown in this study, self-adhesive resin cements experienced large delayed polymerization that continued up to 24 hours, and probably 7 days according to recent studies.¹⁸ Therefore, sufficient time is needed to properly evaluate the polymerization of self-adhesive resin cements. Also, the self-curing potential of self-adhesive resin cements might be understated if it is evaluated at 10-30 minutes after polymerization, as reported in previous studies.^{16,19,20}

On the contrary, Maxcem Elite showed high Rp max in the self-cure mode, which resulted in higher DC compared with M 4-20 group at 10 minutes, and DC was even higher than the M 2-20 group at 24 hours after polymerization (p < 0.05; Table 4; Figure 4). This high self-curing potential of Maxcem Elite has already been described in previous studies, and higher amounts of self-curing components than other self-adhesive resin cements and use of an amine-free redox initiator system were suggested as possible explanations. 16,19 Although a definitive explanation has not been given due to a lack of information from the manufacturers, such high selfcuring potential of Maxcem Elite seems to be suitable to obtain rapid polymerization in cases with gold or zirconia crowns, where there is little chance for light activation of the cement.

An attenuated total reflectance (ATR) accessory has been used with a Fourier transform infrared spectrometer in most studies on the polymerization kinetics of resin composite. 12,16,20-28 However, only the surface layer of the resin specimen (approximately 1-2 µm) can be analyzed in the ATR setting. When considering that the polymerization level can vary depending on the location within a layer of dual-cure resin cement, 29 ATR may not be the best method to assess the overall quality of the resin cement layer. Therefore, in this study, the infrared beam path was designed to penetrate the full thickness of the resin cements. For this purpose, near-IR, with greater penetration, was selected instead of mid-IR, and the specimen was mounted on a holder at a 45° vertical angle to avoid blockage of the IR path by the light-curing tip (Figure 1). In this method, the IR beam penetrates the overlying ceramic block and the resin cement layer. However, it is well known that ceramic does not alter the infrared spectrum, although it does reduce the intensity, 30 and we could not find any disturbance of the IR spectrum by the ceramic interposition compared with the background spectrum.

CONCLUSIONS

Within the limitations of this study, the following conclusions could be made. For both conventional and self-adhesive dual-cure resin cements, insufficient light exposure (20 seconds of light-curing time) through thick ceramic restoration (4 mm thick) resulted in a DC even lower than that of self-curing alone.

Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

(Accepted 2 May 2016)

REFERENCES

- Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, & Leloup G (2006) A physico-chemical explanation of the post-polymerization shrinkage in dental resins *Dental Materials* 22(5) 405-412.
- Leprince JG, Palin WM, Hadis MA, Devaux J, & Leloup G (2013) Progress in dimethacrylate-based dental composite technology and curing efficiency *Dental Materials* 29(2) 139-156.
- Leprince JG, Lamblin G, Devaux J, Dewaele M, Mestdagh M, Palin WM, Gallez B, & Leloup G (2010) Irradiation modes' impact on radical entrapment in photoactive resins Journal of Dental Research 89(12) 1494-1498.
- Meng X, Yoshida K, & Atsuta M (2008) Influence of ceramic thickness on mechanical properties and polymer structure of dual-cured resin luting agents *Dental Materials* 24(5) 594-599.
- Manhart J, Chen H, Hamm G, & Hickel R (2004) Buonocore Memorial Lecture. Review of the clinical survival of direct and indirect restorations in posterior teeth of the permanent dentition *Operative Dentistry* 29(5) 481-508.
- Lee IB, & Um CM (2001) Thermal analysis on the cure speed of dual cured resin cements under porcelain inlays Journal of Oral Rehabilitation 28(2) 186-197.
- Lee IB, An W, Chang J, & Um CM (2008) Influence of ceramic thickness and curing mode on the polymerization shrinkage kinetics of dual-cured resin cements *Dental Materials* 24(8) 1141-1147.
- 8. Stansbury JW, & Dickens SH (2001) Determination of double bond conversion in dental resins by near infrared spectroscopy *Dental Materials* **17(1)** 71-79.
- Yamasaki LC, De Vito Moraes AG, Barros M, Lewis S, Francci C, Stansbury JW, & Pfeifer CS (2013) Polymerization development of "low-shrink" resin composites:

- Reaction kinetics, polymerization stress and quality of network *Dental Materials* **29(9)** e169-e179.
- Salehi S, Gwinner F, Mitchell JC, Pfeifer C, & Ferracane JL (2015) Cytotoxicity of resin composites containing bioactive glass fillers *Dental Materials* 31(2) 195-203.
- Bacchi A, Consani RL, Martim GC, & Pfeifer CS (2015)
 Thio-urethane oligomers improve the properties of light-cured resin cements *Dental Materials* 31(5) 565-574.
- 12. Oliveira M, Cesar PF, Giannini M, Rueggeberg FA, Rodrigues J, & Arrais CA (2012) Effect of temperature on the degree of conversion and working time of dual-cured resin cements exposed to different curing conditions *Operative Dentistry* **37(4)** 370-379.
- 13. Feng L, Carvalho R, & Suh BI (2009) Insufficient cure under the condition of high irradiance and short irradiation time *Dental Materials* **25(3)** 283-289.
- 14. Feng L, & Suh BI (2007) Exposure reciprocity law in photopolymerization of multi-functional acrylates and methacrylates *Macromolecular Chemistry and Physics* **208(3)** 295-306.
- Musanje L, & Darvell BW (2003) Polymerization of resin composite restorative materials: Exposure reciprocity Dental Materials 19(6) 531-541.
- Moraes RR, Boscato N, Jardim PS, & Schneider LF (2011)
 Dual and self-curing potential of self-adhesive resin cements as thin films Operative Dentistry 36(6) 635-642.
- Ferracane JL, Stansbury JW, & Burke FJ (2011) Selfadhesive resin cements: Chemistry, properties and clinical considerations *Journal of Oral Rehabilitation* 38(4) 295-314.
- Baena E, Fuentes MV, Garrido MA, Rodriguez J, & Ceballos L (2012) Influence of post-cure time on the microhardness of self-adhesive resin cements inside the root canal *Operative Dentistry* 37(5) 548-556.
- 19. Arrais CA, Chagas CL, Munhoz A, Oliveira M, Reis AF, & Rodrigues JA (2014) Effect of simulated tooth temperature on the degree of conversion of self-adhesive resin cements exposed to different curing conditions *Operative Dentistry* **39(2)** 204-212.
- 20. Aguiar TR, Di Francescantonio M, Arrais CA, Ambrosano GM, Davanzo C, & Giannini M (2010) Influence of curing mode and time on degree of conversion of one conven-

- tional and two self-adhesive resin cements *Operative Dentistry* **35(3)** 295-299.
- 21. Archegas LR, de Menezes Caldas DB, Rached r N, Soares P, & Souza EM (2012) Effect of ceramic veneer opacity and exposure time on the polymerization efficiency of resin cements *Operative Dentistry* **37(3)** 281-289.
- 22. Arrais CA, Giannini M, & Rueggeberg FA (2009) Kinetic analysis of monomer conversion in auto- and dual-polymerizing modes of commercial resin luting cements *Journal of Prosthetic Dentistry* **101(2)** 128-136.
- 23. Arrais CA, Rueggeberg FA, Waller JL, de Goes MF, & Giannini M (2008) Effect of curing mode on the polymerization characteristics of dual-cured resin cement systems *Journal of Dentistry* **36(6)** 418-426.
- 24. Frassetto A, Navarra CO, Marchesi G, Turco G, Di Lenarda R, Breschi L, Ferracane JL, & Cadenaro M (2012) Kinetics of polymerization and contraction stress development in self-adhesive resin cements *Dental Mate*rials 28(9) 1032-1039.
- 25. Moraes RR, Brandt WC, Naves LZ, Correr-Sobrinho L, & Piva E (2008) Light- and time-dependent polymerization of dual-cured resin luting agent beneath ceramic *Acta Odontologica Scandinavica* **66(5)** 257-261.
- Passos SP, Kimpara ET, Bottino MA, Santos GC, Jr., & Rizkalla AS (2013) Effect of ceramic shade on the degree of conversion of a dual-cure resin cement analyzed by FTIR Dental Materials 29(3) 317-323.
- 27. Tezvergil-Mutluay A, Lassila LV, & Vallittu PK (2007) Degree of conversion of dual-cure luting resins lightpolymerized through various materials *Acta Odontologica Scandinavica* **65(4)** 201-205.
- 28. Yan YL, Kim YK, Kim KH, & Kwon TY (2010) Changes in degree of conversion and microhardness of dental resin cements *Operative Dentistry* **35(2)** 203-210.
- 29. Puppin-Rontani RM, Dinelli RG, de Paula AB, Fucio SB, Ambrosano GM, & Pascon FM (2012) In-depth polymerization of a self-adhesive dual-cured resin cement *Operative Dentistry* **37(2)** 188-194.
- Fuller RM, Rathbun DG, & Bell RJ (1968) Transmittance of cer-vit glass-ceramic in the ultraviolet, visible, infrared, and submillimeter wavelength regions Applied Optics 7(6) 1243-1244.