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Degree of Conversion of Etch-and-Rinse and Self-etch Adhesives Light-cured Using QTH or LED

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Clinical Relevance

The effect of QTH and LED curing lights on the degree of conversion of bonding agents is material dependent.

SUMMARY

In the current study, the degree of conversion (DC) of bonding agents photoactivated using QTH or LED light-curing units (LCUs) was evaluated by Fourier Transform infrared spectroscopy with an attenuated total reflectance (ATR) device. Four LCUs were evaluated: one QTH (Optilux 501; Demetron Kerr) and three LEDs: Radii Cal (SDI), Elipar FreeLight 2 (3M ESPE) and Bluephase (Ivoclar Vivadent). Two etch-and-rinse (Scotchbond Multi-Purpose–SBMP and Single Bond 2–SB2) and two self-etch adhesives (Clearfil SE Bond–CSE, and Clearfil S^3 Bond–CS3) were tested. For SBMP and CSE, the primer was not used. The irradiance and spectral emission of the LCUs were obtained with a radiometer and spectrometer. The materials were placed onto the ATR cell as thin films, the solvent was evaporated (when necessary) and photoactivation was carried out for 20 seconds. The DC (%) was evaluated after five minutes (*n*=5). The data were statistically analyzed (*p*<0.05). The irradiance for Optilux, Radii, FreeLight 2 and Bluephase was 760, 600, 1000 and 1100 mW.cm^{-2}, respectively. The wavelength of emission for Optilux was between 375 and 520 nm (peak at 496 nm), while for Radii, it was

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between 420 and 520 nm (peak at 467 nm). Freelight 2 presented an emission spectrum between 415 and 520 nm, and for Bluephase, it was between 410 and 530 nm, both having a peak at 454 nm. SB2 generally showed higher DC compared with the other bonding agents. When cured using the QTH unit, the DC results were SB2=CS3>CSE>SBMP; for all LEDs, the DC results showed SB2>CSE>SBMP>CS3. For SB2, the highest DC was observed when the material was cured with Radii, while there were no significant differences among the other LCUs. CSE and CS3 showed higher DC when cured using the QTH unit, but similar results were observed among the LEDs. For SBMP, no significant differences among the LCUs were detected. In conclusion, the combination bonding agent vs curing unit had a significant effect on DC, mainly for the self-etch adhesives.

INTRODUCTION

The impact of strong adhesive bonds to dental hard tissues in the long-term clinical performance of composite restorations is still controversial. Several factors may affect longevity of the bonds, including the nature of the bonding agent and proper polymerization of the material. *In vitro* studies have indicated a good relationship between the degree of conversion (DC) and the mechanical properties of the adhesive with the strength of bonding to tooth tissues.[1-3] A high DC may also reduce permeability at the bonding assembly,[4] increasing the resistance to degradation.[5-6] Incomplete polymerization of adhesive monomers has been speculated as one of the reasons for the occurrence of nanoleakage.[6]

Dental adhesive agents contain (di)methacrylates that polymerize under irradiation with visible light.[7] Camphorquinone (CQ) is the most widely used photosensitizer in light-cured dental materials, with an absorption peak at 468 nm.[8] For many years, quartz-tungsten-halogen (QTH) bulbs have been used as the main dental light-curing unit (LCU) for photopolymerization. These LCUs generate a relatively broad spectra of wavelengths, usually between 370 and 520 nm.[9] This wide spectrum embraces the absorption range of most photoinitiators used in adhesive systems.[10-11] However, some factors may compromise the performance of QTH units, such as fluctuation in the line voltage, long-term degradation of the bulb and filter, contamination of the light guide, damage to the fiber-optic bundle and bulb overheating within the unit.[12-13]

On the other hand, the use of light-emitting diodes (LEDs) is increasingly popular among clinicians. LEDs consume little power and do not require filters to produce blue light.[12,14] The semiconductors used for light emission, instead of the hot metal filaments in QTH bulbs, generate less internal heat and undergo little degradation over time.[14] The main difference in the emission radiation is the narrower spectrum of wavelengths of the LEDs, usually centered at 470 nm.[14] Investigators are still evaluating the effectiveness of LED technology for the photopolymerization of dental composites.[15-16] However, adhesives usually present different comonomers as compared with resin composites, and they may also present organic solvents, which can affect polymerization. Despite these differences, the effect of LCUs on the DC of adhesive systems has seldom been evaluated.[7,17]

The current study evaluated the effect of one QTH and three LED LCUs on the DC of four commercial adhesives systems. The null-hypothesis tested was that the type of LCU would not impact the DC of the different systems.

METHODS AND MATERIALS

Four commercially available, light-cured adhesives systems were tested: Scotchbond Multi-Purpose (SBMP, 3M ESPE, St Paul, MN, USA), Single Bond 2 (SB2, 3M ESPE), Clearfil SE Bond (CSE, Kuraray Co, Ltd, Osaka, Japan) and Clearfil S^3 Bond (CS3, Kuraray Co, Ltd). Classification, manufacturer and composition of all the materials are listed in Table 1. The DC of the bonding agents was measured using

Table 1: *Classification, Manufacturer and Composition of the Bonding Agents Used in This Study*

Bonding Agent	Classification*	Manufacturer	Composition*
Scotchbond Multi-Purpose**	Three-step, etch-and-rinse	3M ESPE, St Paul, MN, USA	Bis-GMA, HEMA, polyalkenoic acid copolymer, CQ, EDMAB, DHEPT
Single Bond 2	Two-step, etch-and-rinse		Bis-GMA, HEMA, DUDMA, polyalkenoic acid copolymer, CQ, DHEPT, water, ethanol, silica
Clearfil SE Bond**	Two-step, self-etch	Kuraray, Osaka, Japan	Bis-GMA, HEMA, 10-MDP, CQ, DHEPT, colloidal silica
Clearfil S^3 Bond	One-step, self-etch		Bis-GMA, HEMA, 10-MDP, CQ, ethanol, water, colloidal silica

**As informed by the manufacturers. **Composition for only the Bond bottle is presented.*
Bis-GMA:bisphenol-A glycidyldimethacrylate; HEMA:2-hydroxyethylmethacrylate; CQ:camphorquinone; EDMAB:ethyl4-dimethylaminobenzoate; DHEPT:dihydroxyethyl p-toluidine; DUDMA: diurethane dimethacrylate; 10-MDP: 10-methacryloyloxydecyl dihydrogen phosphate.

Fourier Transform mid-infrared spectroscopy (Prestige21; Shimadzu, Tokyo, Japan), equipped with an attenuated total reflectance (ATR) device. The ATR device is composed of a horizontal ZnSe crystal, with a 45° mirror angle (Pike Technologies, Madison, WI, USA). Constant volume of the adhesive resin was placed on the horizontal face of the ATR cell, where total internal reflection occurs, as previously described.[18] For SBMP and CSE, only the bond agent was tested, that is, the primer bottle was not used.

A support was coupled to the spectrometer to hold the LCU and standardize a 5-mm distance between the light guide tip and material. Four LCUs were evaluated: one QTH (Optilux 501; Demetron Kerr, Orange, CA, USA) and three LEDs: Radii Cal (SDI, Bayswater, Victoria, Australia), Elipar FreeLight 2 (3M ESPE) and Bluephase (Ivoclar Vivadent, Schaan, Liechtenstein). The irradiance of each LCU was measured with a calibrated power meter (Ophir Optronics, Jerusalem, Israel), and the spectral distribution was analyzed using a computer-controlled spectrometer (USB2000; Ocean Optics, Dunedin, FL, USA). For the solvated adhesives SB2 and CS3, the solvent was evaporated for five seconds using a low-pressure air stream. The diameter of the specimens was restricted to match the diameter of the light guide. Before photoactivation, a Mylar strip was placed over the adhesive to avoid inhibition of the polymerization by oxygen. The resulting thickness of the specimen was ~20 µm.

A preliminary reading for the unpolymerized material was taken under the following conditions: 32 scans co-addition, 1900–1400 cm^{-1} frequency range, 4 cm^{-1} resolution, Happ-Genzel apodization and 2.8 mm.s^{-1} mirror speed. Photoactivation was then carried out for 20 seconds. Although differences in irradiance among the LCUs generated unequal radiant exposures, the photoactivation time was kept constant to better simulate clinical conditions. The spectrum of the cured specimens was obtained five minutes after light-activation. The DC (%) was evaluated in the absorbance mode using a baseline technique,[19] 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}, as previously described.[18] Five specimens were tested for each group. The data were submitted to two-way ANOVA (bonding agent *vs* LCU). All pairwise multiple comparison procedures were performed by the Student-Newman-Keuls' method (p<0.05).

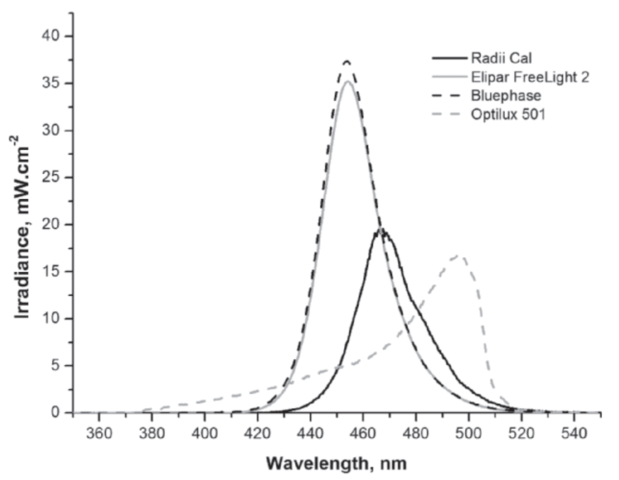

Figure 1. *Light spectrum profiles emitted by the LCUs. The wavelength of emission for Optilux 501 was between 375 and 520 nm (peak at 496 nm), while for Radii Cal, it was between 420 and 520 nm (peak at 467 nm). Elipar Freelight 2 presented an emission spectrum of between 415 and 520 nm, and Bluephase presented an emission spectrum of between 410 and 530 nm, both having a peak at 454 nm.*

RESULTS

Characterization of the LCUs

The irradiance measured for Oplitux 501, Radii Cal, Elipar FreeLight 2 and Bluephase were 760, 600, 1000 and 1100 mW.cm^{-2}, respectively. The light spectrum profiles emitted by the LCUs are shown in Figure 1. The wavelength of emission for QTH Optilux 501 was between 375 and 520 nm, with an emission peak on the curve at 496 nm. Radii Cal showed a wavelength of emission between 420 and 520 nm, with an emission peak at 467 nm. Elipar Freelight 2 presented an emission spectrum between 415 and 520 nm, with an emission peak at 454 nm. The wavelength of emission for Bluephase was between 410 and 530 nm, with a peak on the curve at 454 nm.

Degree of Conversion

The results for DC are shown in Table 2. The factors "bonding agent" (p<0.001) and "LCU" (p<0.001) were

Table 2: *Means (SD) for Degree of Conversion (%) Testing the Different Light-Curing Units*

	QTH	LEDs		
Bonding Agents	**Optilux 501**	**Radii Cal**	**Bluephase**	**Elipar Freelight2**
Scotchbond Multi-Purpose	59.3 (1.1) ^{A,c}	57.9 (0.5) ^{A,c}	57.1 (0.4) ^{A,c}	58.6 (0.4) ^{A,c}
Single Bond 2	79.9 (1.3) ^{B,a}	84.5 (2.1) ^{A,a}	78.9 (2.8) ^{B,a}	78.3 (4.0) ^{B,a}
Clearfil SE Bond	74.1 (1.4) ^{A,b}	65.5 (0.4) ^{B,b}	64.8 (0.4) ^{B,b}	64.7 (0.5) ^{B,b}
Clearfil S^3 Bond	77.1 (1.1) ^{A,a}	44.4 (4.1) ^{B,d}	45.4 (2.7) ^{B,d}	43.0 (0.8) ^{B,d}

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

significant, as well as their interaction ($p<0.001$). The power of the test performed for all sources of variation was 1. Irrespective of the LCU, SB2 generally showed significantly higher DC, compared with the other bonding agents. When cured using the QTH unit, the DC for SB2=CS3>CSE>SBMP. On the other hand, for all the LEDs tested, the DC results showed SB2>CSE>SBMP>CS3. For SB2, the highest DC was observed when the material was cured with Radii Cal ($p<0.001$), while there were no significant differences among the other LCUs ($p\geq0.431$). In contrast, CSE and CS3 showed significantly higher DC when cured using the QTH unit ($p<0.001$), while for both materials, similar results were observed among the LEDs ($p\geq0.142$). For SBMP, no significant differences among the LCUs were detected ($p\geq0.29$).

DISCUSSION

The current results indicate that the LCUs had a material-dependent effect on the DC of the adhesive agents. Thus, the null-hypothesis tested was rejected. According to the manufacturers, all the materials evaluated in this study had CQ as photoinitiator, which absorbs a wide spectrum of wavelengths from 360 nm to 510 nm, with an absorbance peak at 468 nm.[11] For effective photopolymerization, spectral irradiance of the LCU has to overlap as much as possible with the absorption spectrum of the photoinitiator.[8,20] Despite differences in irradiance levels, the LEDs presented higher irradiance concentrated around 468 nm than the QTH unit. Thus, one could expect higher DC values for the LEDs. Nonetheless, the self-etch adhesives CSE and CS3 presented significantly higher DC when light-activated using the QTH source.

One possible explanation for the above results was reported by Chen and others.[8] The authors showed the absorption peak of CQ decreases as the light continues to shine, and the absorption curve of CQ is dislocated to 400 nm in the later stage of the photoactivation process. During photoreaction, the trimethylnorcamphane part of the CQ structure remains unchanged; this part is probably responsible for the short-wavelength absorption of the CQ molecule. Shifting the absorption peak wavelength of CQ might favor the curing promoted by QTH sources, which have broader emission spectra; the narrow light emitted by first and second generation LEDs may not excite the trimethylnorcamphane part of CQ. However, alteration in the absorption profile of CQ may occur at long exposure times; hence, it is questionable whether a 20-second period of light-activation is sufficient for this effect to occur.

Another point to be observed is that the absorption peak of CQ may shift when the molecule is dissolved in water and solvents.[21] This might have occurred primarily for the hydrophilic adhesive CS3, impairing its polymerization with LCUs presenting narrow spectra.[21] In addition, hydrophilic bonding agents with higher water concentration tend to present lower DC.[22-23] For SB2, although the bonding solution is dissolved in ethanol and water, no interference in polymerization was observed. Lower water content and different co-monomer polarity[21] for SB2 may explain this finding not affecting polymerization using the LED units.

No significant differences among the LCUs were observed for the non-solvated SBMP. This finding is probably related to the high viscosity of this adhesive, thus further restricting the mobility of radicals and monomers. Non-solvated adhesives as SBMP and CSE generally present high viscosity due the presence of high molecular weight monomers, mainly Bis-GMA.[24] Despite the similar viscosity of SBMP and CSE,[24] the former does not present fillers in its composition, as does the latter, suggesting a higher content of Bis-GMA for SBMP.[24] A higher content of a dimethacrylate may render this material as having a greater ability to form crosslinks, which may also interfere with further conversion.[1] Polymer crosslinking reduces the diffusion of reactants at the latter stage of the reaction, causing a rapid onset of reaction-diffusion-controlled termination, ultimately reducing the extent of conversion.[25] The fact that, irrespective of the irradiance, all LCUs yielded a similar conversion for SBMP, suggests that a DC of around 58% may reflect the maximum conversion extent for this adhesive under the conditions tested in the current study.

The same light-activation period was used for all materials and LCUs, regardless of their irradiance level. Therefore, different radiant exposures were delivered to the samples. The manufacturers of adhesives systems indicate one specific exposure time for their materials, not taking into account differences among LCUs. Thus, experimental designs using a constant light-activation time are important to more accurately simulate clinical conditions. Despite the differences in irradiance levels, the results for each adhesive agent were generally similar among the LCUs. The LED Radii Cal, however, although having lower irradiance, showed similar and sometimes improved photopolymerization potential, when compared with the other LEDs. This finding might be related to the emission peak of Radii being more consistent with the absorption peak of CQ. In addition, the polymerization potential of both the self-etch adhesives was affected by the narrow LED lights. As both self-etch agents are from Kuraray, it remains unknown whether the presence of other photosensitizer(s) not informed by the manufacturer may explain this finding.

Conversion measurements have been widely used to provide a relative assessment of the quality of dental adhesives and to correlate to their bond strengths.[1,3-4,6,26-28] However, because DC is known to not provide a complete characterization of polymer, other analyses should be used to provide a more in-depth assessment of the network structure.[1] In addition, DC was evaluated five minutes after light-activation and it is assumed that bonding assemblies might be placed approximately at this time under occlusal loads. It is uncertain, though, whether the DC could increase over longer periods, as the literature presents contrasting findings regarding the increase in conversion over the course of time.[17,28]

The polymerization process of adhesive resins is dependent on many factors, such as monomer structure and functionality,[1] viscosity,[1,24] temperature[24] and the presence of solvents.[10,22-23,27] Thus, the current study did not aim to compare the DC among the bonding agents, but rather the effect of the LCUs for each system. The current results indicate that the impact of QTH and LED lights on the DC of bonding agents was material-dependent. The combination bonding agent *vs* curing unit had a significant effect on the DC of the adhesives tested. The manufacturers should provide information, such as minimal irradiance and the time required for optimal light-activation of their adhesive systems, taking into account the increasing use of LED lights by clinicians.

CONCLUSIONS

Within the limitations of the current study, the following conclusions can be drawn:

- The combination bonding agent *vs* curing unit had a significant effect on the degree of conversion of the adhesives tested;
- The polymerization potential of both self-etch adhesives was affected by the narrow LED lights;
- Despite the lower irradiance level, the LED with an emission peak more centered at 468 nm showed similar and sometimes improved photopolymerization potential compared to the other LEDs.

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