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## ORIGINAL ARTICLE

# Degree of conversion of three fissure sealants cured by different light curing units using micro-Raman spectroscopy

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**KEYWORDS**degree of conversion;  
fissure sealants;  
light-curing units;  
Raman spectroscopy

**Abstract** *Background/purpose:* Monomer to polymer conversion is important for optimal mechanical properties and resistance to biodegradation of resin-based materials. Incomplete conversion of fissure sealants may account for lower retention and fracture resistance as well as elution of leachable components. The objective of this study was to determine the degree of conversion (DC) of three fissure sealants cured using a conventional quartz-tungsten halogen (QTH) or a high power light-emitting diode (LED) light-curing unit using micro-Raman spectroscopy.

*Materials and methods:* Delton Opaque and Helioseal Opaque and Helioseal Clear were applied to 60 noncarious permanent molars and cured with the QTH or the LED. Micro-Raman spectra were obtained from the top and the bottom surface of each sample. Three-way analysis of variance ( $\alpha = 0.05$ ) was used for data analysis.

*Results:* Top surface DC values were significantly higher than bottom surface in each material irrespective of the light-curing unit ( $P < 0.05$ ). LED produced significantly higher DC values than the QTH with all three materials ( $P < 0.05$ ). Helioseal Opaque showed significantly lower DC values than Helioseal Clear ( $P < 0.05$ ). DC values for Delton and Helioseal Clear were comparable ( $P > 0.05$ ).

*Conclusion:* Higher DC is achieved with the LED with less exposure time compared with the conventional QTH at top and bottom surfaces of the three fissure sealants, although a lower conversion may be expected in opaque materials.

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## Introduction

Dental caries remains one of the most common preventable diseases in children,<sup>1</sup> with the occlusal surfaces of the first and second permanent molar teeth being particularly susceptible.<sup>2</sup> The use of resin based fissure sealants (FSs) is widely recommended.<sup>3</sup> These contain resin monomers similar to those found in resin-based composites (RBCs). Two types of FSs are commonly available, i.e., clear and opaque, representing alternatives to the formula of the material.

Material composition, monomer to polymer conversion, and reaction kinetics are important parameters that determine the loss of mechanical function and leaching of components from all types of RBC materials in the clinical situation.<sup>4</sup> The shade of RBC materials is known to have a significant effect on the polymerization of resin.<sup>5,6</sup> Light (photons) is absorbed by darker shades and diffused by the white pigments in light opaque shades, compromising the degree of conversion (DC) of RBCs, and similar phenomena occur in FSs.<sup>7</sup> The opacity of FSs is due to the incorporation of opacifiers, which, because they reflect, scatter, and absorb light, will bring about a decrease in light energy that penetrates the FS. Therefore, it can be expected that polymerization may be affected within the bulk of the FS material as a function of depth.

In the recent past, various types of high-intensity light-curing units (LCUs) with outputs of 1000 mW/cm<sup>2</sup> have been marketed to obtain increased depth of cure for RBCs with a concomitant reduction in clinical time. Currently, quartz tungsten halogen (QTH) and light emitting diodes (LED) are the most commonly used LCUs. A previous study on FSs showed that 10 seconds of curing with either a high intensity QTH LCU or an LED LCU achieved an equivalent monomer to polymer conversion to a 20-second cure with a conventional QTH LCU.<sup>8</sup> An earlier study compared ultraviolet (UV)-activated versus visible light-cured FSs using infrared spectroscopy.<sup>9</sup> The literature lacks data on the DC of opaque versus clear FSs as well as the changes in monomer to polymer conversion across material depth as a function of light source.

Monomer conversion has been measured by several different methods,<sup>10–12</sup> and recently with micro-Raman spectroscopy.<sup>13,14</sup> Micro-Raman spectroscopy is a noninvasive technique that requires little sample preparation, and it analyses the chemical composition of various biologic and synthetic materials. It has been employed in dentistry to identify tooth tissue mineral components, effect of treatment modalities, polymerization rate of various materials, and tooth tissue/material interfaces, as well as the effect

of sample preparation, storage conditions, and light curing regimes.

The aim of the present study was to assess whether the DC, determined by micro-Raman spectroscopy, of clear and opaque FSs is influenced by two different types of curing lights, i.e., an LED or a QTH LCU. The null hypothesis was that there is no significant difference in the top and bottom DC values for the three FSs when cured by either an LED or a QTH LCU.

## Materials and methods

A total of 60 noncarious permanent molar teeth were extracted during the provision of routine orthodontic treatment in the Orthodontic Department of the Edinburgh Dental Institute in Edinburgh, UK. The age range of the patients was 10 to 16 years. Written, informed consent was obtained from all patients for the use of the teeth in the present study. Ethical approval was granted by the Ethics Committee, Lothian NHS Board, Edinburgh, UK.

The teeth were cleaned with an ultrasonic scaler to remove debris, polished with pumice and a rubber cap using a slow speed handpiece and rinsed under tap water for 30 seconds, after which they were stored in 0.12% thymol solution for not more than 3 months prior to use. Prior to the application of the FS, the tooth cusps were reduced by not more than 1 mm to create a flat surface using a high-speed handpiece with a diamond bur. The teeth were randomly allocated to Groups I–VI ( $n = 10$ ) using computer-generated numbers. Table 1 lists the materials used in the present study.

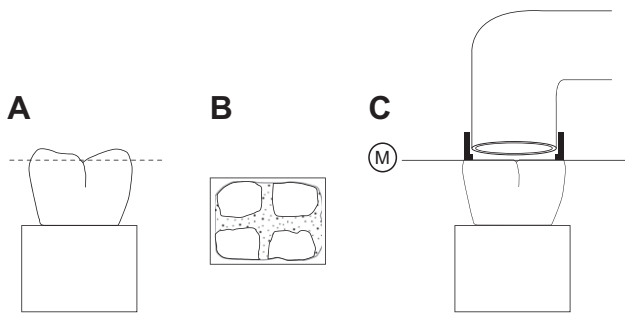
In accordance with both of the manufacturers' recommendations, enamel was etched with 37% phosphoric acid for 30 seconds, rinsed with water for 10 seconds and dried by a gentle, dry stream of air until a chalky white appearance was obtained, prior to placement of the sealant.

The FS was placed in fissures up to the level of the flattened cusps, care being taken to eliminate any trapped air. A Mylar strip was placed on top of the FS, which was then cured with either a QTH LCU (Prismetics Lite; Dentsply, Detrey, Konstanz, Germany) for 20 seconds or an LED LCU (bluephase; Ivoclar Vivadent, Schaan, Lichtenstein) for 10 seconds in accordance with the manufactures' instructions. The tip-to-surface distance was standardized to 1 mm using a custom-made light guide (Fig. 1). The light intensity of both the QTH LCU and the LED LCU was monitored by a blue phase light meter (Ivoclar Vivadent, Schaan, Lichtenstein). Throughout the study the mean (SD) light intensity for the QTH LCU and the LED LCU was 503(35) and

**Table 1** Fissure sealants used in the present study.

Material	Code	Manufacturer	Composition
Delton Opaque	DEL OP	Dentsply Ltd, Surrey, UK	Aromatic and aliphatic dimethacrylate monomers, ethyl-p-dimethyl-aminobenzoate, titanium dioxide, silicon dioxide, initiators
Helioseal Opaque	Hel OP	Ivoclar Vivadent, Schaan, Lichtenstein	Bis-GMA, TEGDMA, titanium dioxide, initiators, stabilizers, catalysts
Helioseal Clear	Hel CL		Bis-GMA, TEGDMA, initiators, stabilizers

GMA = bisphenol A-glycidyl methacrylate; TEGDMA = Triethylene glycol dimethacrylate.



**Figure 1** Standardization of a light-curing unit tip-to-surface distance. (A) Tooth embedded in acrylic resin block. Cusp reduced by not more than 1 mm to create a flat surface; (B) the fissures filled with fissure sealant to the level of the flattened cusps; (C) mylar strip (M) placed over the uncured fissure sealant and the tip-to-surface distance standardized to 1 mm using a custom-made light guide.

1568 (46), respectively. Placement and curing were done at  $22 \pm 2^\circ\text{C}$  and relative humidity was 32%–36%, as monitored by USB-502 data logger (Measurement Computing, Norton, MA, USA). The curing regime for each group was as follows: Group I, Delton cured with QTH LCU; Group II, Delton cured with LED LCU; Group III, Heliaseal OP cured with QTH LCU; Group IV, Heliaseal OP cured with LED LCU; Group V, Heliaseal CL cured with QTH LCU; And Group VI, Heliaseal CL cured with LED LCU.

Using a water-cooled, slow-speed diamond saw, (Isomet, Buehler; Lake Bluff, IL USA) teeth were subsequently sectioned vertically, first through the middle of the fissure and then 2 mm buccally to produce a 2-mm thick specimen. The more lingual surface, produced by section A-A<sub>1</sub> was polished by wet grinding with a 400, 600, and 1200 grit silicone carbide discs. Following this, each specimen was reduced to a manageable size by two sections along the long axis of the tooth and a final section parallel to the occlusal surface, resulting in specimens approximately 4 mm × 2 mm × 2 mm (Fig. 2).

The thickness of the FS was measured in triplicates using a digital caliper (Jade products, Rugby, UK) along a line perpendicular from the flat surface of the FS to the deepest

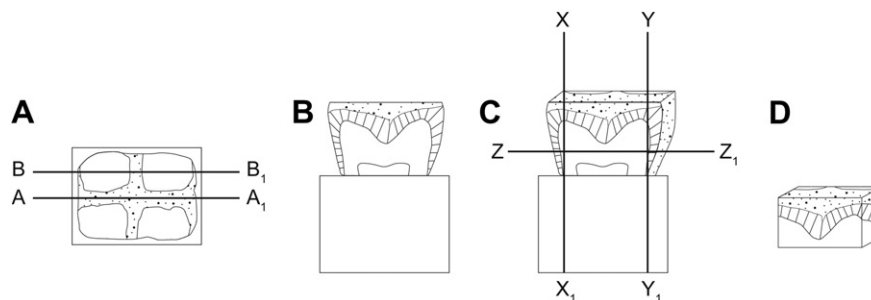
part of the fissure. The time taken from curing the FS to completion of preparation never exceeded 15 minutes; immediately after preparation, all specimens were placed in distilled water in a sealed container maintained at  $37 \pm 1^\circ\text{C}$  in a water bath and stored in the dark for 24 hours.

After the 24-hour storage period, Micro-Raman spectroscopy was performed using LABRAM 300 (HORIBA Jobin Yvon Ltd, Stanmore, Middlesex, UK). Fig. 3 shows the micro-Raman spectrometer and the prepared specimen on the stage prior to capturing spectra. The micro-Raman spectrometer was first calibrated for zero and then coefficient values using a silicon sample. Spectra were taken using the following micro-Raman parameters: 20 mW HeNe laser with 632.817 nm wavelength, spatial resolution  $\sim 1.5 \mu\text{m}$ , spectral resolution  $\sim 2.5 \text{ cm}^{-1}$ , slit 300  $\mu\text{m}$ , confocal hole 500  $\mu\text{m}$ , filter 100%. The laser beam was initially focused with a  $\times 10$  objective, while the spectra were finally obtained with a  $\times 100$  objective lens (Olympus UK Ltd, London, UK). Complementary LabSpec4.18 software was used for data analysis (HORIBA Jobin Yvon Ltd, Stanmore, Middlesex, UK).

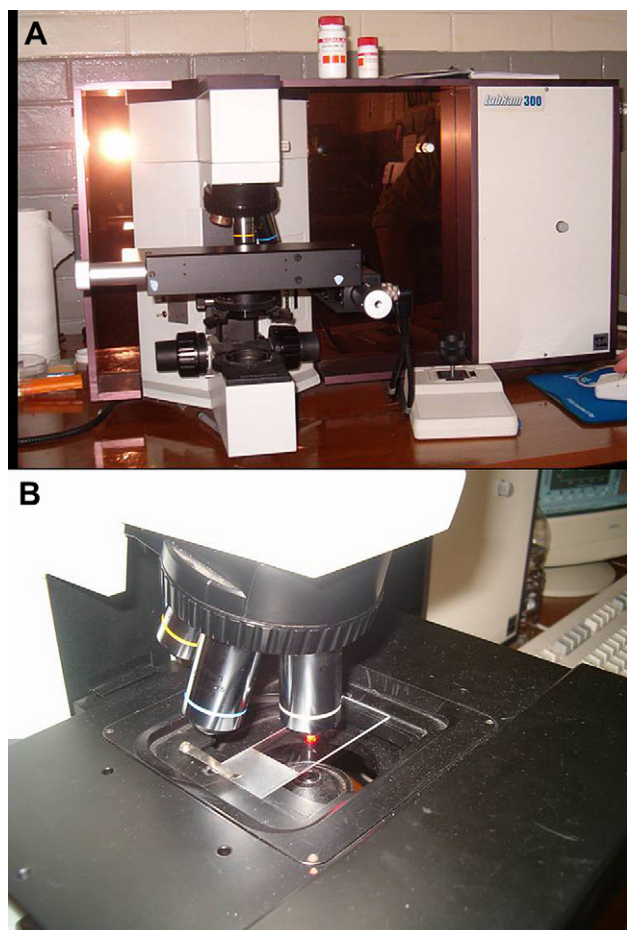
Three-point spectra were taken at random positions within a zone more than 10  $\mu\text{m}$  but less than 20  $\mu\text{m}$  from the top of each specimen. Similarly, three-point spectra were obtained at the bottom of each specimen within a 10- $\mu\text{m}$  zone from the fissure-enamel junction. Each spectrum was taken with a 10-second accumulation time and 10 acquisitions. Spectra obtained from unpolymerized FSs were taken as reference. Postprocessing of spectra was performed using the dedicated software LabSpec4.18 (HORIBA Jobin Yvon Ltd) and included the band fitting procedure using the Levenberg-Marquardt method of nonlinear peak fitting for the best fit.

The DC was calculated according to the following formula,  $\text{DC} = (1 - R_{\text{cured}}/R_{\text{uncured}}) \times 100$ , where  $R$  is the ratio of aliphatic and aromatic peak intensities at  $1639 \text{ cm}^{-1}$  and  $1609 \text{ cm}^{-1}$  in cured and uncured FSs.

Data satisfied the assumptions required for the use of analysis of variance [ANOVA] (independent samples; Gaussian distribution by Kolmogorov-Smirnov test,  $P > 0.15$ ; Bartlett's test for equal variance,  $P > 0.05$ ). Data were statistically analyzed using three-way ANOVA at a 0.05 significance level (Minitab 15; Minitab Inc., State College,



**Figure 2** Preparation of samples for Raman spectroscopy. (A) A 2-mm thick specimen was prepared by first making a vertical section A-A<sub>1</sub> through the middle of the fissure, mesio-distally, and then a second section B-B<sub>1</sub>, buccal to this; (B) surface prepared by section A-A<sub>1</sub> was polished by wet grinding and shows the fissure sealant on top of enamel; (C) to produce a conveniently small specimen for Raman spectroscopy, two sections were made, X-X<sub>1</sub> and Y-Y<sub>1</sub>, both in the long axis of the tooth and 4 mm apart. A final section Z-Z<sub>1</sub> perpendicular to the long axis of the tooth and parallel to the surface of the fissure sealant produced a specimen 4 mm × 2 mm × 2 mm; (D) this shows the final specimen 4 mm × 2 mm × 2 mm. Raman spectra are taken from the polished surface and from the top edge of the fissure sealant vertically down onto the enamel.



**Figure 3** (A) Raman spectroscope; (B) specimen on stage prior to taking spectra.

PA, USA). The factors were material (three levels: Hel CL, Hel OP, Delton), position (two levels: top and bottom) and LCU (two levels: QTH and LED). The interaction term material\*position\*LCU was tested to determine whether the effect of each factor was consistent at different levels of other factors. Since the interaction between these factors was not significant ( $P = 0.064$ ), the effect of each factor was interpreted separately.

## Results

The means (SD) of the thickness of the FS in each group ( $n = 10$ ) were Delton QTH 1.09 (0.27) mm; Delton LED 1.20 (0.30) mm; Helioclear Opaque QTH 1.19 (0.34) mm; Helioclear Opaque LED 1.21 (0.32) mm; Helioclear Clear QTH 1.17 (0.25) mm; and Helioclear Clear LED 1.14 (0.28) mm. Bartlett's test for equal variance showed that the differences among the standard deviations (SDs) were not significant ( $P = 0.9357$ ). The Kolmogorov-Smirnov test indicated that all groups showed a Gaussian distribution. The data met the assumptions required and were analyzed by ANOVA at the level of significance ( $\alpha = 0.05$ ). There was no statistically significant difference in the thickness of FS between the groups ( $P = 0.9472$ ).

**Table 2** Mean, SD, and CIs for the degree of conversion at top and bottom surfaces of the three fissure sealants.<sup>a</sup>

Material	Mean (SD)	Upper 95% CI	Lower 95% CI
HEL QTH top	81.9 (1.4)	82.4	81.3
HEL QTH bottom	77.9 (4.6)	79.6	76.2
HEL LED top	83.3 (3.9)	84.7	81.2
HEL LED bottom	81.7 (3.1)	82.9	80.6
DEL QTH top	84.8 (3.5)	86.1	83.4
DEL QTH bottom	79.8 (7.4)	82.6	77.1
DEL LED top	86.1 (4.4)	87.7	84.4
DEL LED bottom	79.1 (5.1)	81.0	77.2
Clear QTH top	84.8 (3.4)	86.1	83.6
Clear QTH bottom	81.8 (6.2)	84.1	79.5
Clear LED top	86.8 (3.1)	88.0	85.7
Clear LED bottom	81.5 (3.3)	82.8	80.3

CI = confidence interval; DEL = Delton; HEL = Helioclear; LED = light-emitting diode; QTH = quartz-tungsten halogen; SD = standard deviation.

<sup>a</sup> values are in %.

Mean (SD) values and confidence intervals for each FS are presented in Table 2. The summary of statistical analysis is given in Table 3.

The LED LCU produced significantly higher DC values than the QTH LCU with all three sealants ( $P = 0.006$ ). The DC value for the top surface was significantly higher compared with the bottom surface of each material when cured with either the QTH or LED LCU ( $P < 0.001$ ). Helioclear Opaque showed significantly lower DC values than Helioclear Clear ( $P < 0.001$ ), but similar to Delton ( $P = 0.069$ ). There was no difference in DC values for Delton and Helioclear Clear ( $P = 0.054$ ).

## Discussion

Based on the obtained results for DC values, the null hypothesis was rejected. Because the thickness of FSs was not statistically different, it was considered acceptable to compare data from the top and bottom of each sample. Although, generally Mylar strips are not used in clinical curing of FSs, they are routinely used in *in vitro* curing of resin-based materials to reduce the variable effect of oxygen inhibition on polymerization. For this reason, they were used in the present study as described in the methods

**Table 3** Summary of the statistical analysis.<sup>a</sup>

Factor		P value	Significance
LCU	QTH vs LED	0.006	S
Position	Top vs Bottom	< 0.001	S
Material	Hel OP vs Del OP	0.069	NS
	Hel OP vs Hel CL	< 0.001	S
	Del OP vs Hel CL	0.054	NS

ANOVA = analysis of variance; DEL = Delton; HEL = Helioclear; LCU = light-curing units; LED = light-emitting diode; NS = not significant; OP = opaque; QTH = quartz-tungsten halogen; S = significant.

<sup>a</sup> Three-way ANOVA with Tukey's post-tests.

and materials section. For a similar reason, the “top” measurements were made within a 10–20- $\mu\text{m}$  subsurface zone.

The cusps were reduced to the level of the FS producing a flat surface, which allowed the use of a custom built light guide to maintain the tip-to-surface distance of 1 mm. This deviates from clinical practice, but it was considered important to standardize the tip to surface distance in this study. Leaving the cusps intact would have introduced an unacceptable variable that could result in a variation in monomer conversion.

Molds have been used previously to study the DC of RBCs.<sup>15</sup> However, the thickness of FSs may allow light to be reflected back from the substrate, in the clinical situation, enamel, affecting the DC at the base of the FS. This would not be the case if a mold had been used. Therefore, it was considered appropriate to use natural teeth and to replicate the clinical situation as closely as possible.

Possible postpolymerization alterations in DC are known to occur even in samples in the dark. Therefore, we followed conventionally accepted methodology by taking micro-Raman measurements after the 24-hour “dark” storage period.<sup>16</sup> On the other hand, it has shown that DC of resin-based materials is not altered during sample sectioning.<sup>15</sup>

QTH LCUs with a light intensity of 450 to 500  $\text{mW}/\text{cm}^2$  for 20 seconds have been conventionally used to polymerize FSs. To reduce clinical curing time, LCUs with much greater power output, such as “second generation” LEDs, as used in the present study, and high output QTHs, have been introduced. Conflicting information exists, however, concerning the ability of these types of LCUs to provide adequate monomer conversion during the polymerization of RBCs and adhesives.<sup>12,17–20</sup> Less has been reported regarding the polymerization of FSs by high power LCUs.<sup>8</sup>

Micro-Raman spectroscopy has been increasingly used to determine the DC of resin-based composite materials.<sup>13–15,21</sup> From the review of the literature it would appear that the present study is the first to use micro-Raman spectroscopy to study monomer conversion in FSs. The use of this non-invasive technique involves the quantification of reacted C = C double bonds or methacrylate groups in cured versus uncured material. In Bis-GMA-based materials this is achieved by comparing the intensity of the aliphatic group peak at  $1640\text{ cm}^{-1}$  to the aromatic group peak at  $1610\text{ cm}^{-1}$ . The latter is used as an internal standard, not being influenced by the polymerization reaction.

Using infrared spectroscopy, Warnock and Rueggeberg<sup>8</sup> evaluated the DC of light-cured FSs using conventional and high power QTH and conventional and high power LED LCUs and compared it with a self-cured FS. A 10-second cure using either a high power QTH or LED LCU provided equivalent conversion to a 20-second cure using the conventional QTH LCU. This is in contrast to the results of the present study, which, using the same exposure times, showed that the high-power LED LCU was significantly better than the conventional QTH LCU. Platt and colleagues<sup>22</sup> concluded that adequate polymerization was dependent on the material and the brand of LCU rather than whether a QTH or LED LCU was used. Caution should always be exercised when comparing different studies as differences in the LCU status or design may give results that do not warrant conclusions being made about whether or

not one curing regime is superior to another. Two papers were found in the literature referring to the DC of commercially available FSs were those by Papagiannoulis and others<sup>9</sup> and Osorio and colleagues.<sup>23</sup> In the former study, the DC was studied in nine commercially available FSs, including Delton and Helioclear, using infrared spectroscopy. The results indicated that UV-cured materials provided the highest DC followed by visible light cured systems. Despite this finding, the clinical failure of UV-cured systems is attributed to stabilization and shelf life problems of the catalyst and the harmful side effects of UV-radiation.<sup>9</sup> In the latter study that used differential scanning calorimetry, the DC of Delton and Helioclear were found to be approximately 45%,<sup>23</sup> which was considerably lower than the 77%–86% DC range reported in the present study using micro-Raman spectroscopy. Again, caution must always be exercised in comparing studies that have used different methodologic approaches.

Previously DC of RBCs, adhesives, and FSs has been determined using the microhardness test, differential scanning calorimetry, or Fourier transform infrared spectroscopy (FTIR).<sup>24–26</sup> It has been shown that although a certain degree of correlation exists between microhardness and the degree of conversion, it is not linear, which calls into question the sensitivity of microhardness tests in evaluating monomer to polymer conversion.<sup>25</sup> This is especially the case in different materials with multiple variables in their chemical composition, making it impossible to distinguish the particular effect of any one variable on the degree of conversion. Differential scanning calorimetry uses the assumption that all methacrylate-based materials release the same amount of heat as lauryl-methacrylate during polymerization. This material is used as reference in calculating monomer conversion introducing a certain limitation in the testing procedure.<sup>27</sup> Infrared or FTIR spectroscopy requires extensive sample preparation and does not allow measurements across material depth *in situ*. Therefore, Raman spectroscopy was used as a nondestructive method with little or no sample preparation that uses the ratio of peak intensity of molecular groups in uncured and cured material in the DC calculation. Uncured material serves as its own control and linear measurements across the sample are possible.

Previous studies have shown that DC values were higher on top versus bottom surfaces in RBCs.<sup>12,28</sup> This was confirmed in the present study for FSs though the thickness of the FSs was considerably less than that quoted for the RBCs in these studies. Helioclear Opaque produced a lower DC than Helioclear Clear and comparable with Delton. Lower DC values can be expected at the base of the FS due to light attenuation as it reflects internally, scatters, and is absorbed by the material.<sup>29</sup> This is in agreement with the study by Yue and colleagues<sup>7</sup> who, when using Knoop hardness test, found greater depth of cure in clear versus opaque FSs.

Light transmittance in FSs may be affected by opacifiers and fillers.<sup>7,30</sup> Shade is also known to affect DC values in RBCs where, in general, darker shades result in lower DCs.<sup>5,6</sup> The manufacturer’s technical data indicate the presence of titanium dioxide as the only difference in the chemical composition of the two Helioclear FSs used in the current study. This, however, does not exclude the possibility of the inclusion of other constituents, not stated by the manufacturer, such as any type of fillers.

The DC values for Delton were between those obtained for Helioclear Clear and Opaque, although they are not significantly different. According to the manufacturer's data, Delton contains about 40 wt% of fillers of unspecified type or size. Fillers are not stated by the manufacturer to be included in either of the Helioclear products. Therefore, it is difficult to arrive at any conclusion as to what causes differences in DC values between the various materials.

The present study suggests that the use of a high power LED LCU for 10 seconds results in higher monomer conversion in FSs compared with a conventional QTH at twice the curing time. The potential for using LED LCUs in pediatric dentistry with a consequent reduction in curing time may be seen as beneficial for the treatment of the dentally anxious and uncooperative child.

Studies have shown that QTH LCUs tend to generate a higher pulp temperature rise than LED LCUs.<sup>12,20</sup> However, Baroudi and colleagues<sup>31</sup> concluded that a potential risk for heat-induced pulp damage might be associated with high power LED sources. The curing of FSs on top of intact enamel seems unlikely to cause a significant pulp temperature rise even in young teeth due to the insulating effect of intervening enamel and dentine.

One of Delton's constituents is bisphenol A-glycidyl methacrylate (Bis-GMA) of which Bis-Phenol A is a degradation product. Adverse hormonal and endocrine reactions have been reported in cell<sup>32</sup> and animal studies.<sup>33</sup> Schmalz and colleagues<sup>34</sup> have reported elution of Bis-Phenol A from Delton up to 24 hours after curing. Further research is required to identify possible adverse effects of Bis-Phenol A originating from FSs in children and young adults.

## Conclusions

The present results suggest that higher monomer conversion is achieved with LED LCUs with less exposure time compared to conventional QTH LCUs at both the top and bottom surfaces of the three studied FSs, although lower conversion may be expected in opaque materials. The shorter and more efficient curing regime of LED LCUs may be considered advantageous in the curing of FSs in clinical pediatric practice.

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