Degree of Conversion and Hardness of a Silorane-Based Composite Resin: Effect of Light-Curing Unit and Depth

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Clinical Relevance

Forty seconds of light exposure in increments up to 3 mm of a novel silorane-based composite resin produced higher degree of conversion and hardness than thicker increments, using halogen or LED units.

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SUMMARY

Purpose: **To investigate the effect of different light-curing units and depths on the degree of conversion (DC) through Fourier transform infrared spectroscopy (FTIR) and Knoop Hardness Number (KHN) of a silorane-based composite resin (Filtek LS, 3M ESPE, St Paul, MN, USA) (LS).**

Materials and Methods: **LS specimens mounted in a particular designed matrix were photoactivated by three light-cure units (LCUs) at depths of 2, 3, 4, and 5 mm. The DC was determined in a FTIR spectrometer with an attenuated total reflectance accessory. The KHN was measured in an automatic microhardness tester. The results were analyzed using the Friedman and Spearman statistical tests (α=0.05).**

Results: **There was no effect of LCUs on the DC (p=0.472) or KHN (p=0.174) for all of the studied depths. The highest DC and KHN means were found at 2-mm depth, which were**

not statistically different from 3-mm depth, but were higher than 4-mm and 5-mm depths (*p*=0.007). Spearman analysis found a positive linear correlation between the variables KHN and DC (*r*=0.858, *p*<0.000).

Conclusions: **The LCUs' effect was not verified. Values of DC and KHN for LS decreased with increasing depth. The highest values for both DC and KHN were obtained at depths of 2-3 mm.**

INTRODUCTION

Direct composite resin (CR) restorations have been widely used in restorative dentistry procedures, in both anterior and posterior regions.[1-4] However, despite the recent innovative improvements in techniques and materials, clinical problems are still observed in CR restorations.[5]

Regarding the materials' properties, polymerization shrinkage stress is still considered to be one of the main drawbacks of CRs.[6] It is dependent on the composite constitution, cavity configuration (C-factor), elastic modulus, and degree of conversion (DC). To reduce the phenomena of volumetric contraction and shrinkage stress during polymerization, studies have sought to change the proportion, size, quantity, and shape of inorganic fillers present in CRs.[7] Other studies analyzed the proportion of organic matrix/inorganic particles and its relationship with the polymerization shrinkage, concluding that an excessive amount of fillers (above 80 wt%) could modify the rheology of the CR, reducing its ability to flow during the initial curing stage (pre-gel state) and increasing the polymerization shrinkage stress and the contraction of the remaining tooth structure.[8-10] Those factors could lead to debonding, microleakage, postoperative sensitivity, marginal discoloration, secondary caries, and/or eventual restorative failures. Another method to minimize the disadvantages of CRs is to modify the chemical structure of the organic matrix used. During attempts to improve the Bis-GMA molecule, different formulations were developed, such as urethane matrix,[1,2,4,11] the

espiro-orthocarbonates with their variations,[12-14] and Ormocer (organic modified ceramic), in which silica particles were inserted into the organic matrix, reducing polymerization shrinkage and increasing the conversion sites.[15,16] More recently, a silorane-based resin composite was established that claimed to present a lower shrinkage rate compared to conventional methacrylate CRs. This material is a combination of a siloxane backbone and oxirane rings. The siloxane block shows high hydrophobicity, and the oxirane rings are responsible for the decrease in volumetric contraction during curing, based on a distinct process: cationic ring-opening polymerization.[17] Studies of silorane-based composites report polymerization shrinkage values less than 1% in volume,[17,18] excellent resistance to bending,[18,19] favorable physicochemical and mechanical properties relative to methacrylate-based composites,[17-20] adequate biocompatibility,[21-25] and satisfactory short-term clinical performance.[26,27]

Adequate polymerization is a crucial factor for the optimization of the physical and mechanical properties of CRs, such as hardness and color stability. For a light-cured resin, such as the silorane CR, the polymerization is influenced, among other factors, by irradiation time, intensity of power, and the type of unit activation (eg, halogen, light-emitting diode [LED]). Factors such as the capacity for conversion of the monomers and its relation with different types of light-curing units (LCUs), depth of cure, and mechanical properties have been discussed for methacrylate CRs.[1,17,28-32] However, silorane CR presents a particular polymerization initiator system based on the cationic opening of the oxirane rings. As the initiation process differs from the conventional and well-established photoinitiation of the methacrylate CR based on camphorquinone, it is important to test the silorane CR under different light sources.

Few studies have determined the degree of conversion for silorane-based composites,[20,33,34] its relation with hardness at different depths,[20,35] or the effect of the light source. This study aimed to evaluate the effect of different light-curing units

Table 1: *Emission Spectrum Measures*			
Light-Curing Units	**Radii-cal**	**Bluephase G2**	**Optilux 501**
Spectral range, nm	420-520 (S)	390-520 (S)	385-515 (S)
	440-480 (M)	380-515 (M)	400-505 (M)
Maximum peak of emission, nm	Peak: 460 (S)	Peak 1: 412 (S), 410 (M)	Peak: 494 (S)
	Peak: 460 (M)	Peak 2: 455 (S), 460 (M)	Peak: (M)[a]
Abbreviations: M, data provided by the manufacturer; S, data found in the present study measured by spectrometer (USB 4000, Ocean Optics, Dunedin, FL, USA). [a] Data not provided by manufacturer.			

Table 2:	Power Density and Energy Density for Specific Regions of Spectrum of Each Light-Curing Unit[a]					
Light-Curing Units Spectrum Characteristics	**Power Density, mW/cm^2**			**Energy Density, J/cm^{2b}**		
	Radii-cal	**Bluephase G2**	**Optilux 501**	**Radii-cal**	**Bluephase G2**	**Optilux 501**
Manufacturers' total spectrum	1200	1200	800-900	48	56	32-36
Study total spectrum	894	1430	832	35.76	57.20	33.28
Spectral range (400-515 nm)	836	1316	805	33.44	52.64	32.20
Spectral range (190-400 nm)	30	66	24	1.2	2.64	0.96
Spectral range (>500 nm)	53	85	43	2.2	3.4	1.72

[a] *Power measured by potentiometer (Ophir 10A-V2-SH, Ophir Optronics LTD, Jerusalem, Israel). Power density (mW/cm^2) = Power (mW) × Area (cm^2). Calculation of power density in each spectral range provided by data analysis software (OriginPro 8.0, OriginLab Corp, Northampton, MA, USA).*
[b] *Energy density for a time of 40 seconds.*

and depths on the degree of conversion by Fourier transform infrared spectroscopy (FTIR) and Knoop Hardness Number (KHN) of a silorane-based composite (Filtek LS, 3M ESPE, St Paul, MN, USA) (LS).

METHODS AND MATERIALS

Design of Experiment and Materials Employed

This *in vitro* experimental study was outlined in four randomized complete blocks. This design allowed for control of unknown sources of variation, with each block containing one combination of each factor being studied. The study factors were the depth of cure at four levels (2, 3, 4, and 5 mm) and the light-curing units RC (LED, Radii-cal, SDI Limited, Bayswater, Australia), BP (LED, Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein), and OP (Halogen light, Optilux 501, Kerr Corp, Orange, CA, USA). The LCUs were previously tested for spectral distribution, irradiance (power density), and energy dose (Tables 1 and 2). The experimental units were specimens (n=48) made of silorane-based composite resin Filtek LS, color A3 (Lot: 9NER; 3M ESPE) (Table 3). The response variables were the degree of conversion and Knoop microhardness.

Characterization of Filtek LS

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were carried out using the same equipment (SDT 2960, TA Instruments, New Castle, DE, USA). Micro-Raman spectroscopy was performed using a spectrometer (IHR550, Horiba Jobin Yvon, Kyoto, Japan). The energy dispersive x-ray spectroscopy (EDX) measurements were performed in a fully automatic sequential fluorescence x-ray spectrometer (ZSX Primus II, Rigaku Corp, Tokyo, Japan).

Specimen Preparation

A matrix consisting of a nylon cylinder with a depth of 3 mm with a central perforation 5 mm in diameter

in the bottom was designed. Three interchangeable rings with a thickness of 1 mm with a central perforation 5 mm in diameter were constructed to be placed into the master cylinder to provide different depths. Specific disks were constructed to guide the tip of each LCU to a distance of 2 mm from the bottom of the first specimen. This matrix was developed in order to separately evaluate the depth of cure of the polymerized resin at each depth, without needing to section the specimens (Figure 1).

For the 5-mm deep specimen, the matrix was placed over a 0.1-mm thick glass plate. Its central perforation was then filled with LS in a single 1-mm thick, 5-mm diameter increment. A 0.1-mm thick cover glass was placed on top, and the piece was subjected to a weight of 1200 g for 20 seconds. For the 4-mm depth, the first interchangeable ring was placed over a glass plate. Its central perforation was filled with LS in a single 1-mm thick, 5-mm diameter increment. A 0.1-mm thick cover glass was placed on top, and the piece was subjected to a weight of 1200 g for 20 seconds. Then, the ring containing the LS was placed into the matrix, from bottom to top. The same

| Table 3:	Material Safety Data Sheet : Filtek LS (3M ESPE)		
Composition		**No. CAS**	**%/Wt**
Silane treated quartz		100402-89-9	60-76
Yttrium trifluoride		13709-49-4	5-15
Bis-3,4-epoxycyclohexylethyl-phenyl-methylsilane		154265-59-5	5-15
3,4-Epoxycyclohexylcyclopolymethylsiloxane		—	5-15
Mixture of other by-products		Mixture	<5
Mixture of epoxy-mono-silanole by-products		Mixture	<5
Mixture of epoxyfunctional di- and oligo-siloxane by-products		Mixture	<5
Mixture of alpha-substituted by-products		Mixture	<5
Abbreviation: CAS, Chemical Abstracts Service			
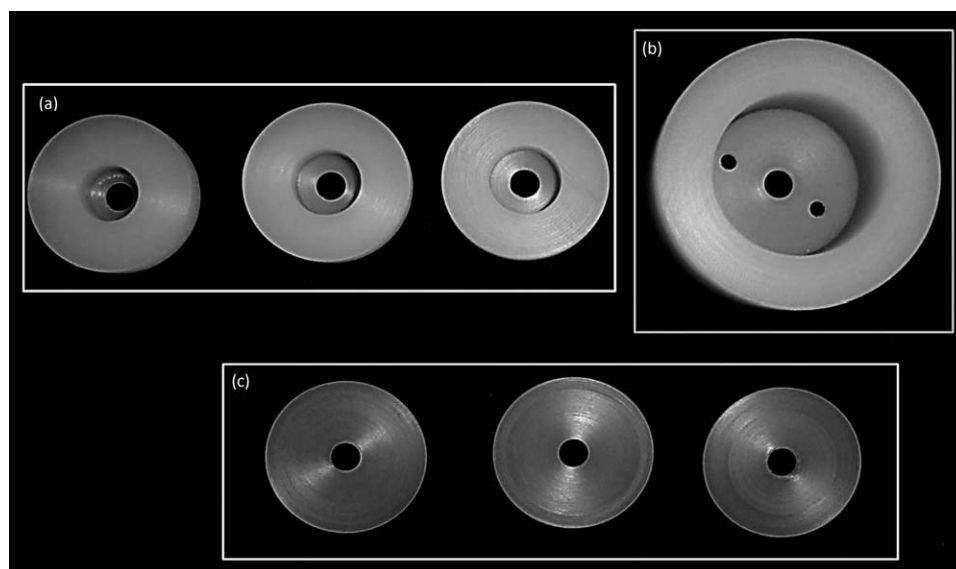
Figure 1. *Matrix used in the study, showing all of its components. (a): Special rings for each light-curing unit. (b): Central cylinder. (c): Interchangeable rings.*

procedure was performed for the 3- and 2-mm depths. The special rings were placed for each LCU, and the set was polymerized for 40 seconds (Figure 2). After photoactivation, the specimens were removed from the nylon matrix, identified (bottom and top), and grouped according to the previous randomization. Then, they were stored at 37°C in the absence of moisture and light for a period of seven days.

Determination of Degree of Conversion

A FTIR spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc, Fitchburg, WI, USA) coupled to a microscope (Centaurus, Thermo Fisher Scientific Inc) and an attenuated total reflectance accessory (Micro-ATR- Ge, Thermo Fisher Scientific Inc) was used. Micro-FTIR spectra in the region of 650-4000 cm^{-1} were collected in absorption mode with a spectral resolution better than 4 cm^{-1} and acquired with 256 accumulations under a dry nitrogen purge. The spectrometer was configured as follows: everglow source, KBr beam splitter, Ge-coated, and HgCdTe detector. Three distinct spectra were measured on the bottom of all 48 specimens. The first was in the center of the specimen, the second was 1.25 mm to the left of the first, and the third was 1.25 mm to the right of the first.

The spectrum of the uncured resin was determined using the previous characterization as a basis for calculating the DC. The bands used as internal standards in this study were a "C-O-C" (883 cm^{-1})
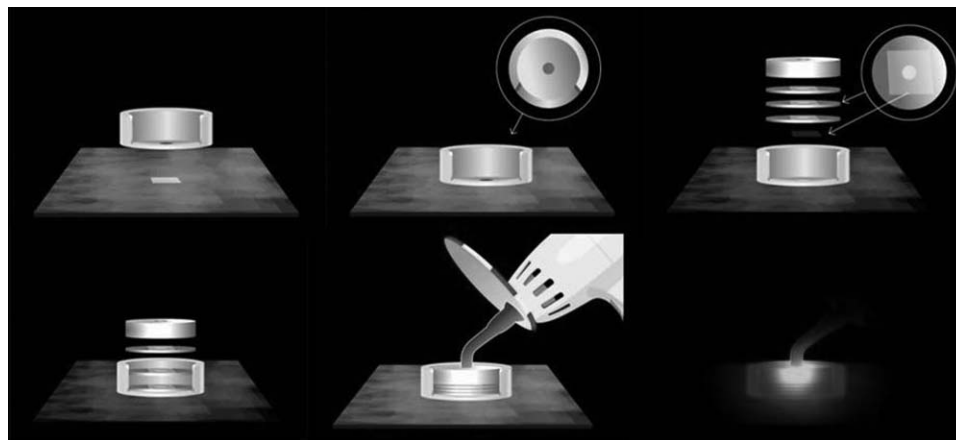

Figure 2. *Representation of the experimental sequence.*

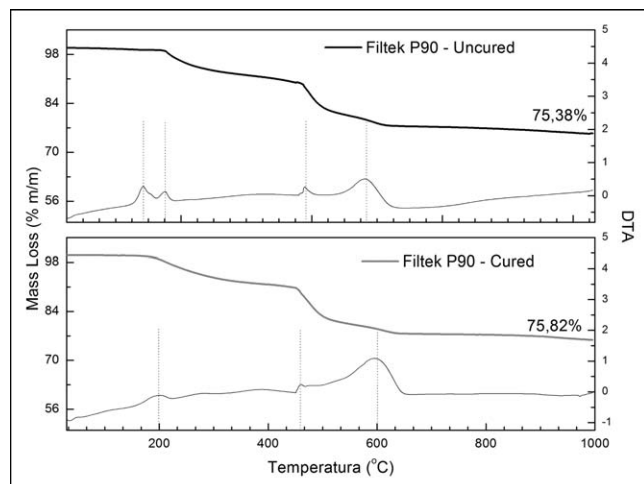Figure 3. *Measures of TG/DTA carried out for cured and uncured LS.*

stretching band and a "C-H" (2919 cm^{-1}) stretching band. The following calculation was performed in order to reach the DC:

$$DC = \left\{ \frac{\left[\left(\frac{AC-O-C}{AC-H} \right)_{UP} - \left(\frac{AC-O-C}{AC-H} \right)_{P} \right]}{\left(\frac{AC-O-C}{AC-H} \right)_{UP}} \right\} \times 100(\%)$$

DC indicates degree of conversion; A, height of the bands; UP, unpolymerized monomer; and P, polymerized monomer.

Determination of Knoop Microhardness

The KHN was determined in an automatic microhardness tester (FM-ARS-9000, Future Tech Corp, Kawasaki, Japan). Five indentations were made on the bottom of the 48 specimens under a force of 50 gf for 50 seconds. The first indentation was located in the center of the sample. The others were located 1.25 mm from the center. The KHN was calculated using the following formula: *KHN = 14229 x P / d²,* where L, P = force (gf) and d = length of long diagonal (μm).

Statistical Analysis

The Kolmogorov-Smirnov test and the Levene test were used to check the normality and the variances equality of data obtained for KHN and DC. As the data did not present a normal distribution, the nonparametric Friedman test was used to evaluate the effect of the individual factors. Spearman correlation test was used to investigate the relationship between the hardness and degree of conversion. A significance level of 5% was utilized for all tests.
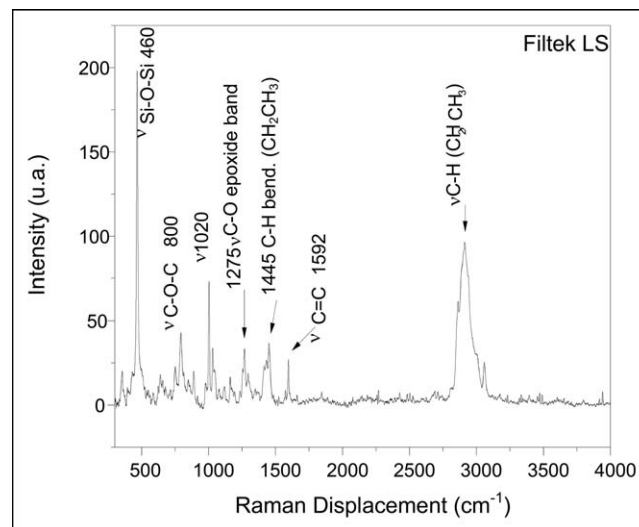

Figure 4. *LS spectrum obtained by Raman spectroscopy.*

RESULTS

Characterization of LS

Thermal analysis revealed a filler/weight ratio of 75.82% (Figure 3). Energy-dispersal x-ray spectroscopy demonstrated the presence of yttrium and iodine as components of the initiation system. Raman spectroscopy qualitatively verified the bands related to the vibrational modes of the epoxy groups and the presence of C=C and C-H bonds (Figure 4).

Determination of Degree of Conversion

DC results for each study factor (depth of cure and light-curing units) in each block were obtained. The Friedman test showed no significant effect (p=0.472) of LCUs on the DC (Table 4). However, a significant effect (p=0.007) was observed when the depths were varied (Table 5). The highest DC mean was found at 2-mm depth, which was not statistically different from 3-mm depth, but was higher than 4-mm and 5-mm depths (p=0.007). The absorbance spectra obtained during the FTIR showed that while the band of the C-H bond (2919 cm^{-1}) remained unchanged (internal standard) after the polymeriza-

Table 4:	Friedman Test to Assess the Effect of Light-Curing Units (LCUs) on the Degree of Conversion of the Filtek LS*		
LCUs	**Blocks**	**Median (Min-Max)**	**Sum of Orders**
Bluephase G2	4	56.94 (32.15-62.12)	11.0
Optilux 501	4	50.79 (33.14-60.08)	7.0
Radii-cal	4	47.29 (37.96-54.40)	6.0
*p=0.472.			

Table 5: *Friedman Test to Assess the Effect of Depths on Degree of Conversion*

Depth, mm	Blocks	Median (Min-Max)	Sum of Orders[*]
2	4	72.85 (65.71-78.66)	16.0[a]
3	4	65.05 (54.61-70.29)	12.0[a,b]
4	4	40.78 (10.27-56.86)	8.0[b,c]
5	4	21.15 (7.08-31.34)	4.0[c]
[*] Values followed by different letters indicate significant difference (p=0.007; least significant difference=7.96).			

tion (Figure 5), a variation in the bands related to the oxirane rings was found (883 cm^{-1}) (Figure 6), suggesting the opening of the oxirane rings.

Determination of Knoop Microhardness

The Friedman test showed no significant effect ($p=0.174$) of the LCUs on the KHN (Table 6). The same test showed a significant effect ($p=0.007$) of depth on the KHN (Table 7). The highest KHN mean was found at 2-mm depth, which was not statistically different from 3-mm depth, but was higher than 4-mm and 5-mm depths ($p=0.007$).

Correlation Between KHN and the Degree of Conversion

Spearman analysis revealed a positive linear correlation between the KHN and DC for LS ($r=0.858$, $p<0.000$) (Figure 7).

DISCUSSION

The physical and mechanical properties of CRs are known to be directly influenced by the degree of
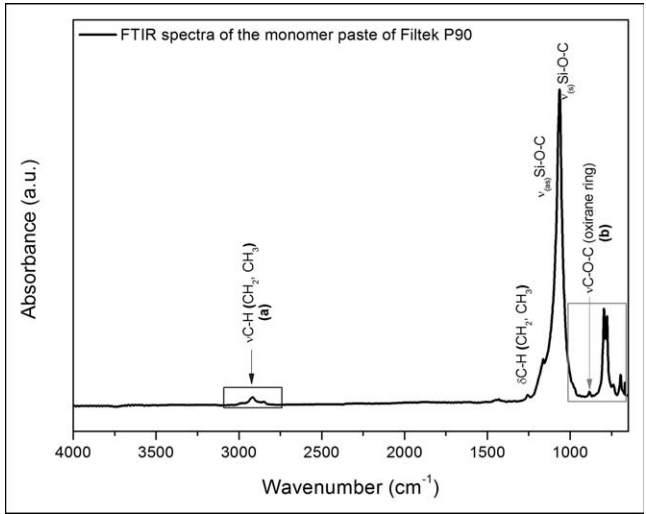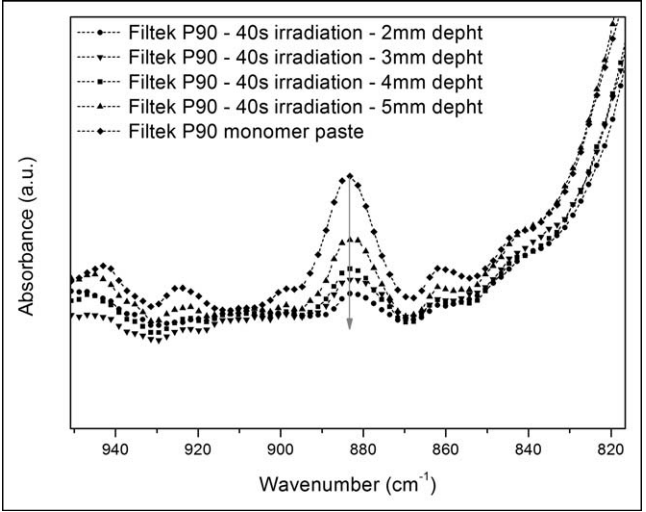

Figure 6. *View the reduction of the band "C-O-C" (883 cm^{-1}) suggesting the opening of the rings in different depths.*

conversion obtained during the polymerization. For methacrylate-based composites, the DC can vary from 43% to 75%, depending on their composition (photoinitiator system, form and amount of particles, and type of organic matrix), the thickness of resin layers, the intensity and spectrum of light radiation, the exposure time, and the distance from the light-curing unit.[31,36,37] More recently, a silorane-based composite resin (LS) was developed and became available on the market. Therefore, it is essential to study the depth of cure of this particular CR.

In the present study, the emission spectrum, power density, and energy emitted by the three LCUs were initially determined in accordance with ISO/TS 10650. The lack of uniformity in the emission spectrum of LCUs reported by manufacturers justifies the need for verification.[20] For the spectral range between 190 to 400 nm and recommended power densities up to 100 mW/cm^2, none of the devices tested exceeded this value. Between 400 and 515 nm, it is recommended that the power density should not be less than 300 mW/cm^2 or more than 1000 mW/cm^2. It was found that only the BP exceeded the recommended values, featuring a power density of

Figure 5. *Identification of bands used to measure the degree of conversion. (a:) Bonding "C-H" (2919 cm^{-1})/internal standard. (b): Band related to the oxirane ring (883 cm^{-1}).*

Table 6: *Friedman Test to Assess the Effect of Light-Curing Units (LCUs) on the Knoop Hardness Number (KHN)[*]*

LCUs	Blocks	Median (Min-Max)	Sum of Orders
Bluephase G2	4	33.10 (27.33-36.88)	11.0
Radii-cal	4	34.66 (28.10-33.71)	7.0
Optilux 501	4	32.69 (27.21-34.28)	6.0
[*] p=0.174.			

Table 7:	*Friedman Test to Assess the Effect of Depth on the Knoop Hardness Number**		
Depth, mm	**Blocks**	**Median (Min-Max)**	**Sum of Orders**[*]
2	4	41.76 (39.98-41.82)	16.0[a]
3	4	38.67 (37.38-38.71)	12.0[a,b]
4	4	33.09 (20.11-34.74)	8.0[b,c]
5	4	20.23 (10.22-24.81)	4.0[c]
* Values followed by different letters indicate significant difference (p= 0.007; least significant difference=7.96).			

1316 mW/cm^2. High levels of photons can generate faster polymerization, impairing CR to flow during the pre-gel state and increasing the stress in the tooth-restoration interface. Above 515 nm, only OP followed the recommendation of up to 50 mW/cm^2, showing a 43-mW/cm^2 power density. None of the light emission spectra of each LCU supplied by the manufacturers was similar to those found by spectroscopic tests in the present study, which may have impacted the power density values. However, there was no influence of LCUs in the two response variables, perhaps because of the 40-second light-curing time, which provided energy density higher than the minimal dose recommended by the manufacturer (20 J/cm^2). Furthermore, DC and KHN are not only dependent on power density but also on the composition of the resin (photoinitiator, type, and size of particles), time of curing, and distance of composite to light source.[7,20,31]

The LS characterization was performed by DTA and revealed a 76% load (weight/weight), which was in accordance with the information provided by the manufacturer. The EDX qualitatively demonstrated the presence of yttrium in the inorganic particles and iodine in the photoinitiator system. These findings reinforce the mechanisms of LS polymerization by opening the oxirane rings with acid cations.[17] Raman spectroscopy was performed to qualitatively verify the bands related to vibrational modes of the epoxy groups and the presence of C=C and C-H bonds. This test would also be used to verify the DC; however, the composite exhibited a luminescence incompatible with the accomplishment.

Some studies have determined the depth of cure of composites by determining DC and hardness.[20,30,35] The DC can be measured by FTIR,[20,30,32-34,38] Raman spectroscopy,[37,39,40] nuclear magnetic resonance,[38] differential scanning calorimetry,[41] and differential thermal analysis.[42] An adequate polymerization of composites is directly related to the DC, providing optimal physical-chemical and mechanical properties as well as satisfactory clinical

performance. In the present study, in order to determine the DC, a nylon cylindrical matrix with a central 5-mm diameter hole, sectioned at four depths separated by 1 mm, was used for specimen preparation. Nylon was chosen to facilitate specimen removal and, because of its similarity to the optical characteristics, reflection and refraction of the dental structures. A specific ring for each LCU was developed to perfectly guide the LCU tip, ensuring the exact depth. The construction of this matrix sectioned at depths of 1 mm aimed to prevent the DC from the heat caused by cutting the specimens.[20] The absorption of water from the cooling process could also change the visualization of the bands during the FTIR analysis.[31]

With respect to the DC of silorane composite, studies have been conducted with distinct objectives using different methodologies, making it difficult to compare the results.[33,34,38,43,44] Only one study assessed the DC, hardness, and the correlation between them at different depths.[20] The present study showed a decrease in the DC as a function of the increased depth, which is in accordance with other studies.[30,34] The mean DC found for the depth of 2 mm in this study was 72.85%, which is higher than the maximum results obtained for silorane composite found in the literature, which ranged from 50% to 64.9%.[33,34,38,43] This difference may be explained by the distinct power densities and curing times selected. As in this present study, the DC did not differ for the 2- and 3-mm depths, and it would be acceptable to use increments of 2 to 2.5 mm as recommended by the manufacturer.

Hardness is an indicator of ductility, smoothness, and abrasion capacity, and may predict the surface wear resistance of a CR.[18] Previous studies that used
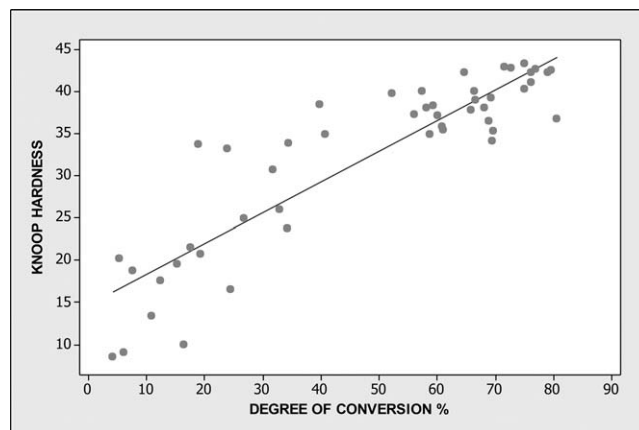

Figure 7. *Scatter diagram of the DC results (%) in the x-axis, plotted as a function of KHN in the y-axis.*

methacrylate composites found that the increase of the amount of inorganic particles by volume produced a high surface hardness and improved the DC.[45] As observed for the DC tests, silorane hardness results are difficult to compare due to methodologic differences.[7,19,20,32,33,35,46,47] The Knoop microhardness mechanical test was used to indirectly determine the depth of cure. This test can be used to measure the hardness of thin regions because the indentation is narrower than that of the Vickers hardness test. Additionally, it is not influenced by the phenomenon of elastic recovery that is common to polymeric materials. A mean KHN of 41.76 was found at the depth of 2 mm. This value is relatively smaller than those found in the literature for methacrylate CRs.[18,47] This can be explained by the low proportion of filler by volume (55%).[18] The KHN results for the silorane composites found in the literature ranged between 43 and 60.[18,47] Similar to the DC, the KHN decreased with depth, and it was significantly higher at a depth of 2 mm compared to 4- and 5-mm depths, but did not differ from 3 mm. A previous study agreed with these results showing that the silorane-based composite was capable of acceptable (80%) bottom-to-maximum microhardness ratios at increments up to 3 mm, at both low and high irradiances.[35] These findings differ from other results[20] that have found no statistically significant difference between the 2- and 6-mm depths using the Vickers microhardness test. This variance in the results may be due to the different hardness tests employed and to the fact that the last study light cured each increment separately.

Similar to the results of another study, a strong correlation was observed between the DC and KHN, which indicated that hardness is a suitable mechanical indicator of DC.[48] Even though there was a positive linear correlation between hardness and DC, it is necessary to further investigate the polymerization process of silorane composites because this material exhibited lower hardness compared to methacrylate composites, even though the DC was acceptable.

CONCLUSION

After 40 seconds of light exposure, different LCUs (halogen or LED) did not affect the DC and KHN of novel silorane-based composite resin at the depths of 2, 3, 4, and 5 mm. Values of DC and KHN decreased with increasing depth. The highest values for both DC and KHN were obtained at depths of 2-3 mm. Although the LS presented a satisfactory degree of conversion, the low Knoop hardness values suggest the need for further studies that address the wear resistance of these materials.

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.

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