Influence of Different Light Sources and Photo-Activation Methods on Degree of Conversion and Polymerization Shrinkage of a Nanocomposite Resin[1]

**S. X. S. Costa[a], L. M. Martins[b], P. A. S. Franscisconi[b], V. S. Bagnato[c], J. R. C. Saad[a],
A. N. S. Rastelli[a, c,]*, and M. F. Andrade[a]**

[a] University of São Paulo State-UNESP, Araraquara School of Dentistry, Department of Restorative Dentistry,
Araraquara, SP, Brazil
[b] University of São Paulo-USP, Bauru School of Dentistry, Bauru, SP, Brazil
[c] University of São Paulo, São Carlos Physics Institute, São Carlos, SP, Brazil
*e-mail: alerastelli@yahoo.com.br
Received June 24, 2009; in final form, July 1, 2009

Abstract—The purpose of this study was to evaluate the influence of different light sources and photo-activation methods on degree of conversion (DC%) and polymerization shrinkage (PS) of a nanocomposite resin (Filtek^{TM} Supreme XT, 3M/ESPE). Two light-curing units (LCUs), one halogen-lamp (QTH) and one light-emitting-diode (LED), and two different photo-activation methods (continuous and gradual) were investigated in this study. The specimens were divided in four groups: group 1—power density (PD) of 570 mW/cm^2 for 20 s (QTH); group 2—PD 0 at 570 mW/cm^2 for 10 s + 10 s at 570 mW/cm^2 (QTH); group 3—PD 860 mW/cm^2 for 20 s (LED), and group 4—PD 125 mW/cm^2 for 10 s + 10 s at 860 mW/cm^2 (LED). A testing machine EMIC with rectangular steel bases ($6 \times 1 \times 2$ mm) was used to record the polymerization shrinkage forces (MPa) for a period that started with the photo-activation and ended after two minutes of measurement. For each group, ten repetitions ($n = 40$) were performed. For DC% measurements, five specimens ($n = 20$) for each group were made in a metallic mold (2 mm thickness and 4 mm diameter, ISO 4049) and them pulverized, prensed with bromide potassium (KBr) and analysed with FT-IR spectroscopy. The data of PS were analysed by Analysis of Variance (ANOVA) with *Welch's* correction and *Tamhane's* test. The PS means (MPa) were: 0.60 (G1); 0.47 (G2); 0.52 (G3) and 0.45 (G4), showing significant differences between two photo-activation methods, regardless of the light source used. The continuous method provided the highest values for PS. The data of DC% were analyzed by Analysis of Variance (ANOVA) and shows significant differences for QTH LCUs, regardless of the photo-activation method used. The QTH provided the lowest values for DC%. The gradual method provides lower polymerization contraction, either with halogen lamp or LED. Degree of conversion (%) for continuous or gradual photo-activation method was influenced by the LCUs. Thus, the presented results suggest that gradual method photo-activation with LED LCU would suffice to ensure adequate degree of conversion and minimum polymerization shrinkage.

1. INTRODUCTION

The polymerization process of a composite resin occurs by the conversion of the monomer molecules of the matrix into a polymer chain, followed by a reduction of the space between these molecules, which then occupy a smaller volume than the initial. This reduction in the total volume of the material is known as the polymerization shrinkage [1]. Although the composite resin is considered the best esthetic direct restorative material, excessive shrinkage of polymerization is one of the main factors that contribute to the failure of restorations [2]. The magnitude of the stress is influenced by several factors, including the overall shrinkage, the curing rate, the elastic modulus, and the stress relieving characteristics of the composite restoration [3].

The determining factors of the polymerization quality is the light power density (mW/cm^2) produced by the light curing unit (LCU). The power density represents the amount of photons emitted in the light guide. A minimal power density of 300 mW/cm^2 is required to effectively polymerize a 2 mm deep increment with a light-curing unit conventional halogen (QTH) and light emitting-diode (LED) [4].

LCUs are an integral part of the daily practice of restorative dentistry. Quartz-tungsten- halogen (QTH), plasma-arc (PAC), argon laser and light-emitting diode (LED) curing lights are currently commercially available and different light sources may also influence the development of physical properties. The QTH curing light has a long, established history as a workhorse for composite resin polymerization in dental practices and remains the most common type of

---

[1] The article is published in the original.

light in use today [5]. The light emitted by these units is generated when the tungsten filament is heated emitting a visible blue light in a large spectrum. A filter limits the interval of the wavelength in the range from 400 to 500 nm (nanometer). Consequently, the use of QTH LCUs to polymerize dental composites has several limitations as the halogen bulbs, reflector and filter degrade over time due to high operation temperatures and heat produced, resulting in a limited effective lifetime of about 40 to 100 h [6−11].

The LCUs using blue light-emitting diode (LED) has the advantage of a narrower spectral range than the QTH light and a better match of light emitted with the absorption spectrum of the photoinitiator camphorquinone [12, 13]. Additionally, LED units do not use filters, which are required with halogen units for wavelength selection. Thus, LED units represent an improvement over halogen lamps [14−18]. According to Aravamudhan et al. (2006) [19] and Calixto et al. (2008) [11], in general, there were no differences between the halogen and LED light-curing units with the same parameters.

In spite of the mechanical properties of current composite resins have been improved, polymerization shrinkage is still an inevitable problem. Polymerization shrinkage and degree of conversion (DC) of resin composites are closely related manifestations of the same process. Ideal dental composite would show an optimal degree of conversion and minimal polymerization shrinkage. These seem to be antagonistic goals, as increased monomer conversion invariably leads to high polymerization shrinkage values [20].

The marginal integrity of composite resins restorations depends on many factors among them the difference between the thermal expansion coefficient of the tooth and the restorative material, however especially the polymerization shrinkage related to the dimethylacrylate-based matrix of these materials. In the polymerization process, composite resins shrink due to their passage from a liquid to solid state and the shrinkage is the result of the reduction in the intermolecular distance between monomeric units. The polymerization shrinkage should be considered as the principal mechanism responsible for problems concerning the interface failures [21, 22].

If shrinkage forces exceed the bonding strength at the interface, the resulting interfacial gap can lead to staining, marginal leakage [23], post-operative sensitivity [24] and recurrent caries [25, 26]. Moreover, the contraction forces can be transferred to neighboring dental structures causing cuspal deflection or fractures in the enamel [27]. The clinical consequences of polymerization shrinkage constitute the main reasons for premature replacement of composite resin restorations [28]. This explains why it is regarded as the main limitation of present-day resin composites and why its elimination or minimization is one of the most important research tasks in this field.

Volumetric contraction and elastic modulus are directly related to the composite degree of conversion [29]. Because higher degree of conversion is also associated with improved mechanical properties [30], there is an idea that high degree of conversion would improve the performance of composite restorations over time. However, it seems reasonable to expect that higher degree of conversion will also lead to higher contraction stresses, therefore, increasing the risk of bonding failure. In fact, a previous study assessing the relationship between degree of conversion and contraction stress in an experimental composite found that the stress development rate increases at higher conversion levels [31].

As a consequence of the dependence of volumetric shrinkage and elastic modulus on degree of conversion (DC), a direct relationship between DC and polymerization shrinkage (PS) exists. Consequently, at this late stage into the polymerization reaction, small increments in DC produce significant increases in PS [31−33]. Furthermore, in vitro studies verified that insufficient conversion may cause allergic reactions and stimulate bacterial growth around restoration margins [34, 35]. Also, residual monomers can act as plasticizers and compromise a composite's mechanical properties [36].

The contraction forces development and relaxation are related to local conditions such as the C-factor corresponding to the bonded/unbonded surface area ratio, structure that dentin exhibits [37−40], the compliance of the substrate corresponding to the surrounding tooth structure and the thickness of the adhesive layer. Also they depend to the composite itself (filler content) [41], ratio and type of comonomers, concentration and system of photoinitiators and finally, to the type of technique used (incremental technique) [42, 43] and parameters of photo-activation (light sources, power densities, photo-activation method) [44].

The photo-activation method has a profound influence on shrinkage stress. High intensity lights provide higher values for degree of conversion, but they also produce higher contraction stress. As lower curing process that permits composite flow may allow for stress relaxation during polymerization [45].

With the objective of to reduce polymerization shrinkage stress different photo-activation methods have been suggested. Commonly, QTH and LED lights have been used in a continuous output mode while emitting a fairly high irradiance [46, 47]. However, radiation from this type of source can also be applied for different methods. The soft-start method, i.e., employs an initial low irradiance for a specific duration followed by a high one equivalent in value to that of the continuous phase [48]. Some studies have associated this method with better marginal integrity of composite resins [47, 49−51].

Table 1. Characteristics of restorative material used in the study (manufacturers' data)

Material	Manufacturer	Shade	Material type	Matrix	Filler size	Filler volume	Lote number
Filtek[TM] Supreme XT	3M/ESPE	A2B	Nanofilled composite	Bis-GMA, Bis-EMA, UDMA, TEGDMA	Agglomerated/non-aggregated of 75 nm silica nanofiller and a loosely bound agglomeratic silica nanocluster consisting of agglomerates of primary silica nanoparticles of 75 nm size fillers. The cluster size range is 0.6 to 1.4	72.5%	6ER

Table 2. Characteristics of light curing units used in the study (manufacturer's data)

Light curing unit/serial number	Manufacturer	Light source	Light curing method (LCM)	Description of LCM
Optilux 501/5817562 USA	Demetron-Kerr	Halogen lamp	Continuous	Power density (PD) of 570 mW/cm^2 for 20 s
			Gradual	PD of 0 at 570 mW/cm^2 for 10 s + 10 s at 570 mW/cm^2
Bluephase/2124 Norway	Ivoclar/Vivadent	LED	Continuous	PD of 860 mW/cm^2 for 20 s
			Gradual	PD of 125 mW/cm^2 for 10 s + 10 s at 860 mW/cm^2

Manufacturers have recommended high light intensity to provide a higher degree of monomer conversion into polymer, thus improving the mechanical properties of composite resins. However, the degree of conversion is always proportionally associated with shrinkage and a high rate of polymerization [52, 53]. Clinically, the effect of post-gel shrinkage and contraction stress can be minimized by flow during setting by applying short pulses of energy (pulse activation) or pre-polymerization at low-intensity light followed by a final cure at high intensity (soft-start techniques) [8, 54], as these methods promote a longer pre-gel phase in light-cured composites. Curing methods using lower irradiance levels were shown to be effective in reducing the rate of stress generation without compromising the conversion of the restorative composite [55].

Some studies have shown that the polymerization rate influences the polymer structure. Thus, so-called soft-start curing may reduce the degree of conversion and, at a given degree of conversion, the crosslink density [56, 57]. It was hypothesized that gradual photo-activation methods would exhibit a reduced crosslink density, in despite of the reduction of the shrinkage. The degree of polymerization in crosslinked polymeric systems plays a potentially large role in determining the ultimate physical and mechanical properties of the material [8].

Thus, in this study it was hypothesized that different light sources and photo-activation methods could lead to different polymer structures and lowest degree of conversion. Since DC and shrinkage properties are correlated, the aim of the present study was to measure the degree of conversion and polymerization shrinkage of a nanocomposite resin photo-activated by QTH and LED LCUs.

2. MATERIALS AND METHODS

2.1. Composite Resin Used in This Study

In the present study, the nano-filled composite resin Filtek[TM] Supreme XT (shade A2B). The Table 1 shows the main composition the dental composite resin used.

2.2. Light-Curing Units Used (LCUs)

Two light-curing units one QTH (Optilux 501/Demetron) and one blue LED (Bluephase/Ivoclar-Vivadent), were used in this study. Two different light-curing methods (continuous and gradual) were tested (Table 2).

Prior to the curing procedures, the output power of the LCUs was measured with a calibrated power meter (Fieldmaster Power Meter, Coherent-model no. FM, set no. WX65, part no. 33-0506, USA) and the diameter of the light guide tip with a digital caliper (Mitutoyo, Tokyo, Japan). Power density (mW/cm^2) was computed as the ratio of the output power and the area of the tip with the following formula: $I = P/A$, where P is the power in milliwatts and A is the area of the light tip in squared centimeters.

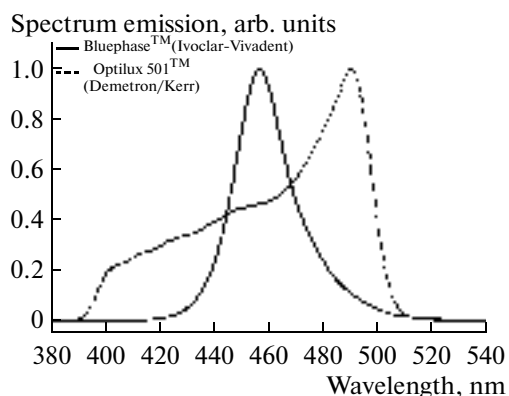Figure 1 shows the emission spectrum of the two LCUs obtained using a spectrophotometer USB 2000 (Ocean Optics).

Spectrum emission, arb. units

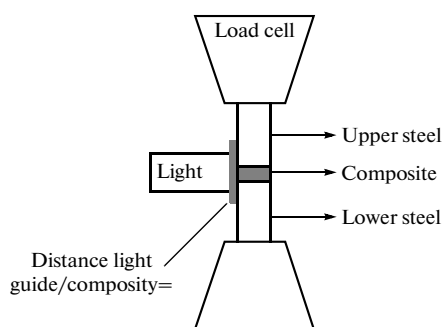

Fig. 1. Emission spectrum of the LCUs.

Fig. 2. Schematic illustration of the steel bases EMIC test system and the light guide of the curing system device.
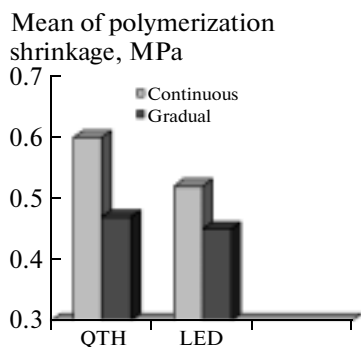

Fig. 3. Averages of the polymerization shrinkage depending of the light source and photo-activation method.

2.3. Samples Preparation

For degree of conversion measurements, the samples ($n = 20$) were made with a metallic mould (4 mm in diameter and 2 mm in thickness). The metallic mould was positioned in a glass plate of 10 mm thickness. The composite resin was packed in a single increment and the top and base surfaces were covered by a mylar strip. A glass sheet with 1 mm thickness was positioned, and the 1 kg weight (kilogram) was used to pack the composite resin. The top surface of the sample was placed in contact with the curing light tip. The samples were photo-activated for 20 s of irradiation times (manufacturer's instructions).

After 24 h, the composite resin was pulverized into fine powder. Five milligrams of the composite powder was thoroughly mixed with one hundred milligrams of KBr (bromide potassium) powder salt. This mixture was placed into a pelleting device and then pressed in a press with a load of 10 t during 1 minute to obtain a pellet. The Table 3 shows the division of the groups.

2.4. Determination of the Degree of Conversion (% DC)

The number of double carbon bonds which are converted in single bonds provides the degree of conversion (%DC) of composite resin. To measure the degree of conversion the pellet was then place into a holder attachment into the spectrophotometer (Nexus-470 FT-IR, Thermo Nicolet, E.U.A). FT-IR spectra of both uncured and cured samples were analyzed using an accessory of reflectance diffuse. The measurements were recorded in absorbance operating under the following conditions: 32 scans, 4 cm^{-1} resolution, 300 to 4000 cm^{-1} wavelength, internal standard before and after curing of the specimen: aromatic $C-C$ (peak at 1608 cm^{-1}). This experiment was carried out in triplicate. The degree of conversion was determined by subtracting the % C=C from 100%, according to the formula:

$$DC(\%) = 1 - \frac{(1638 \text{ cm}^{-1}/1608 \text{ cm}^{-1})\text{cured}}{(1638 \text{ cm}^{-1}/1608 \text{ cm}^{-1})\text{uncured}} \times 100.$$

The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm^{-1}) against.

2.5. Polymerization Shrinkage

The polymerization shrinkage was recorded by a universal testing machine (EMIC, DL 500 BF-NO5775-NS168, São José dos Pinhais, PR, Brazil). Two opposite and parallel stainless steel plates were used (6 × 1 × 2 mm). The bottom plate (cylindrical) was fixed and connected to a Bencor Multitest device especially adapted for this test. The top plate (rectangular) was connected to a 20 kgf load cell of a computerized testing machine (Figs. 2 and 3).

The dental composite resins were placed between the plates (Fig. 3) and the test was performed simultaneously to the composite resins photo-activated record the shrinkage forces for a period that started with the photo-activation and ended after two minutes of measurement. The LCUs was positioned in a device for maintaining a stable position and distance during the test. For each group, 10 repetitions were performed (Table 3).

The tip of the light curing units (LCUs) were placed perpendicularly to the long axis and centred on the middle of the specimen. The distance between the light tip and the composite surface was 1 mm.

During test, the shrinkage stress generated by polymerizing caused a minimal deflection in load cell, which was transmitted to the universal testing machine. Each measurement produced a graph (force, in Newton X time, in seconds). The maximum shrinkage stress obtained for each group was recorded.

2.6. Statistical Analysis

The data of polymerization shrinkage were statistically analyzed by Analysis of Variance (ANOVA) with Welch's correction and Tamhane's test. The DC's data were analysed by Analysis of Variance (ANOVA), using a confidence interval of 95%.

3. RESULTS

3.1. Degree of Conversion

The Table 5 shows the degree of conversion (DC%) mean values promoted by different light-curing units (LCUs) and photo-activation methods. The Analysis of Variance (ANOVA) showed that the DC% was not influenced by photo-activation methods ($p < 0.05$), but differences were observed for light sources. Significant differences were found only when QTH LCU was used, i.e., the QTH provided the lowest values for DC% (Fig. 4).

The DC (%) values varied from 46.21 (±3.03) to 49.35% (±2.28) for QTH LCU photo-activated for continuous and gradual methods, respectively. For LED LCU, the DC (%) values varied from 52.32 (±0.67) to 52.30% (±1.14) when continuous and gradual methods were used.

After 24 h, using the irradiation time recommended by the manufacturers, QTH (20 s) and LED (20 s) were statistically different ($p > 0.001$). Therefore, the results revealed that the light source used had a significant ($p < 0.05$) impact on the degree of conversion.

3.2. Polymerization Shrinkage

Mean values and standard deviations (SD) for polymerization shrinkage (PS) are shown in Table 4. It was observed that there is greater variability of the values of PS for the QTH in relation to those obtained with LED.

The Analysis of Variance (ANOVA) with Welch's correction showed that the polymerization shrinkage was not influenced by LCUs (QTH or LED), but significant differences were found between the two photo-activation methods ($p < 0.001$). The Tamhane's test indicates that the gradual photo-activation

Table 4. Mean (M) and standard deviation for PS

Light source	Photo-activation method	Mean	*	SD
Halógena	Continuous	0.60	b	0.07
	Gradual	0.47	a	0.04
LED	Continuous	0.52	b	0.01
	Gradual	0.45	a	0.01

* Different letters denotes significant difference ($p < 0.05$).

Table 5. Mean (M) and standard deviation (SD) for degree of conversion

Light source	Photo-activation methods	M	*	SD
QTH	Continuous	46.21	a	3.03
	Gradual	49.35	a	2.28
LED	Continuous	52.32	b	0.67
	Gradual	52.30	b	1.14

* Different letters denotes significant difference ($p < 0.05$).

method provided the lowest values for polymerization shrinkage, regardless of the LCU used (Fig. 3).

4. DISCUSSION

Adequate polymerization or high degree of conversion is a crucial factor in obtaining optimal physical properties and the clinical performance of composite resins. Thus, inadequate polymerization leads inferior physical properties, the solubility in the oral environment, and an increased microleakage with a resultant recurrent decay and pulpal irritation [58]. On the other hand, polymerization shrinkage is considered a major problem with resin-based materials because it creates destructive stresses when the material is bonded to cavity walls [59].
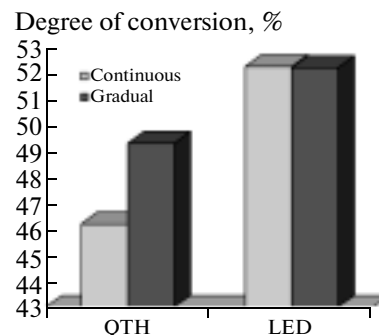

Fig. 4. Averages of the degree of conversion depending on the light source and photo-activation method.

Polymerization shrinkage and degree of conversion of composites are closely related manifestations of the same process. Ideally, composite resins would show a high degree of conversion and minimal polymerization shrinkage. These seem to be antagonistic goals, as increased monomer conversion invariably leads to high polymerization shrinkage values [60].

The contraction stress developing in composites during polymerization depends on many factors such as: the chemical composition of the polymer matrix, filler particles and silane, the rheology and viscosity of the paste, the flow behavior of the material during the pre-gel phase as well as the duration of the pre-gel phase and the initiator systems. In the pre-gel phase, the polymer chains formed are very flexible so that material of the free surface of the cavity can flow. The viscosity of the developing polymer is still low, so that shrinkage stress can be compensated for. The time at which the material is no longer able to compensate for polymerization shrinkage (time until gelation) therefore, determines the final stress in the material [61].

A higher degree of conversion, which is primarily related to curing light intensity and irradiation time, conflicts with the objective of achieving optimal marginal integrity, because of increased shrinkage [62]. To minimize shrinkage stress, "soft cure" or "soft-start" methods were suggested. These photo-activation methods have the option of operating with an initial period of low intensity illumination, which should reduce stress development during composite curing [29, 63].

The use of gradual photo-activation methods to reduce shrinkage stress has become widespread in restorative dentistry. However, an increased susceptibility to ethanol degradation of polymers formed by gradual photo-activation was reported. Asmussen, Peutzfeldt (2001, 2003) [56, 63] and Benetti et al. (2009) [64] explains that a slow polymerization start with low intensity is associated with relatively few centers of polymer growth, resulting in a more linear polymer structure with relatively few crosslinks. On the other hand, a high intensity during the initial phase of the irradiation period will initiate a multitude of growth centers and a polymer with higher cross-link density results.

In agreement with previous observation, the results obtained for Gonçalves et al. (2006) [65] suggest that when low irradiances or gradual methods are used, a relatively high radiant exposure is necessary to originate a polymer network structure similar to that obtained by continuous high irradiance photo-activation.

In the present study, both degree of conversion and polymerization shrinkage were used to estimate crosslinking density of a resin composite photo-activated by two different light sources (QTH and LED) and photo-activation methods (continuous and gradual). For the polymerization shrinkage (PS), statistical difference was observed among the curing methods, independently of the light source used. The continuous method provided the highest values for PS. These findings coincide with the results of Cunha et al. (2006) [66] and Lopes et al. (2008) [10], which found that the conventional mode with QTH and LED LCUs produced the higher stress means. Several authors have reported the efficacy of low intensity or pulse-delay methods in reducing the polymerization contraction stress of composites [10, 54, 60, 67].

For Visvanathan et al. (2007) [68] it is probable that the effects of soft-start method depends on the type of the device used, i.e., LED or QTH and the light intensity, which was not found in this study. This is probably associated to the similar power density between the LCUs, a fact that was not seen in the first LED generations, which had a much lower power density when compared to the halogen-lamp devices. The high light intensity or power density of LCUs used in this study caused fast polymerization with a very short pre-gel phase. As a consequence, the contraction strain occurring in the material during polymerization could not be compensated for by flow and therefore, allowed the development of contraction stress. This statement is in accordance with Ilie et al. (2005) [61] and Tonegawa et al. (2009) [69].

Photo-activation methods tested in the present study did not affect the degree of conversion of the composite resin, in accordance with results of other studies [49, 54, 60, 70, 71].

In this research, the Fourier Transformer Infra-red Spectroscopy analyzes (FT-IR) was used to evaluate a possible interference in the DC% of composite resin produced by the light source and photo-activation method (continuous and gradual). Techniques such as Fourier Transform Infra-red spectroscopy (FT-IR) [29, 72], spectroscopy RAMAN [73], electron paramagnetic resonance (EPR) [74], nuclear magnetic resonance (NMR) [75], differential scanning calorimetry (DSC) [76] and differential thermal analysis (DTA) [77] have been used to determine the DC. Among these, FT-IR is the most frequently used technique.

Asmussen and Peutzfeldt (2003) [63] showed that a lower DC is associated with softer polymers after storage in ethanol. This is in accordance with earlier work [78, 79]. Low DC implies a less dense structure of the polymer and therefore easier penetration of plasticizing substances such as ethanol. Lovell et al. (2001) [80], however, showed contradictory results. They found that the mechanical properties were insensitive to the rate of polymerization but strongly dependent on the final double bond conversion.

However, the DC was influenced by light source. The QTH provided the lowest values for DC. Similar results from a study of Bala et al. (2005) [81], where a LED LCU polymerization was superior to that of QTH LCU. This result can be explained because the

blue LED is almost totally absorbed by the material along the polymerization procedure, producing uniform curing without compromising the physical and chemical properties of the material through time [82].

Several studies reported that the DC of composite resin produced by the QTH was higher than that produced by LED LCUs due to higher light intensities [6, 63]. Other studies reported that LED LCU cured better than did the QTH LCU [14, 83]. However, those studies did not investigate DC in the soft-start method produced by high powered LED LCUs. In this study, DC produced by QTH LCU show a significant statistical difference for both photo-activation methods ($p > 0.001$). However, polymerization produced by high power LED (continuous or gradual photo-activation methods) produced the highest DC. Calixto et al. (2008) [11] showed that, in general, there were no differences in the curing depth between the QTH and LED light-curing units used with the same parameters.

For dental resins cured under clinical conditions, final conversion is typically between 55 and 75% [73, 84], which also agrees with the DC observed in this study, except for the gradual method. Under these circumstances, the DC were 47 and 45% when QTH (gradual method) and LED (gradual method) were used, respectively. Nevertheless, according Soares et al. (2007) [85] and Rastelli et al. (2008) [58] the minimum DC for a clinically satisfactory restoration has not yet been precisely established. A negative correlation of in vivo abrasive wear depth with DC has been found for values in the range of $55-65\%$. This suggests that, at least for occlusal restorative layers, DC values below 55% may be contraindicated [29]. From our experiment, the DC ranged from ±46 to $\pm52\%$.

In this study, composite polymerization by QTH LCU in the continuous photo-activation method produced a DC of 46.21 and 49.35% for gradual photo-activation method, with possible influence on composite physical properties. However, composite polymerization by LED produced DC of 52.32% (continuous method) and 52.30% (gradual method). Thus, according to these results, it seems that the LED-based devices allow for a better conversion from monomers to polymers.

The high power LED LCU is an alternative to the halogen light LCU, because the LED is more compact, wireless and has a working lifetime of more than 10 000 h, which is a significantly lower thermal emission, and LEDs have wavelength peaks of around 470 nm, which match the absorption peak of the most commonly used photo initiator camphoroquinone [7, 86].

A lower degree of conversion could affect the longevity of the composite restoration, because an incomplete conversion may result in unreacted monomers, which might dissolve in a wet environment. In addition, reactive sites (double bonds) are susceptible to hydrolization or oxidation and, thereby, lead to a degradation of the material [58]. Additionally, this fact could directly affect biocompatibility of the composite restoration [87], since increasing the DC number of methacrylate pendant groups available for hydrolytic degradation decreases. Hydrolytic degradation and oxidation of composites may lead to the leaching of different degradation products from composite resin. Formaldehyde has been identified as one of the degradation products. Methacrylic acid has also been identified as an eluted species that can cause irritation of the mucosa membrane and is cytotoxic [58].

The degree of conversion is an important parameter in determining the final physical, mechanical and biological properties of composite resins, since it has been demonstrated that resin composite properties tend to improve as the degree of conversion attained during photo-activation is increased. However, constrained shrinkage during polymerization densification generates polymerization shrinkage stress, which is one of the most significant concerns during the highly technique-sensitive clinical placement of composite restorations.

5. CONCLUSIONS

The results obtained for this study indicate that the photo-activation methods (continuous and gradual) evaluated promoted differences in the polymerization shrinkage, regardless of the light source used. The gradual photo-activation method provided the lowest polymerization shrinkage. However, the degree of conversion was influenced by light source. The light-curing unit based halogen lamp provided the lowest values for degree of conversion, either continuous or gradual photo-activation methods.

Based on the results of this study may be suggested that LED LCU promotes better conversion of the nanocomposite. Additionally, the gradual photo-activation method should be used to minimize the polymerization shrinkage of the material when the LED LCUs second generation are selected due to the high power density.

REFERENCES

1. C. S. Delfino, C. S. C. Pfeifer, R. R. Braga, M. N. Youssef, and M. L. Turbino, Appl. Phys. B **96**, 79 (2009).

2. J. L. Ferracane, Dent. Mater. **21**, 36 (2005).

3. J. L. Ferracane and J. C. Mitchem, Am. J. Dent. **16**, 239 (2003).

4. S. H. Zanchi, R. V. Carvalho, S. A. Rodrigues, Jr., F. F. Demarco, and L. H. Burnett, Jr., Braz. Oral. Res. **20**, 137 (2006).

5. K. S. Vandewalle, H. W. Roberts, and N. Miniotis, J. Esthet. Restor. Dent. **18**, 161 (2006).

6. K. D. Jandt, R. W. Mills, G. B. Blackwell, and S. H. Ashworth, Dent. Mater. **16**, 41 (2000).

7. K. Nitta, Dent. Mater. **21**, 217 (2005).

8. M. S. Soh, A. U. J. Yap, and K. S. Siow, Oper. Dent. **29**, 317 (2004).

9. Q. Ye, Y. Wang, K. Williams, and P. Spencer, J. Biomed. Mater. Res. A **80**, 444 (2007).

10. L. G. Lopes, E. B. Franco, J. C. Pereira, and R. F. L. Mondelli, J. Appl. Oral. Sci. **16**, 35 (2008).

11. L. R. Calixto, D. M. Lima, R. S. Queiroz, A. N. S. Rastelli, V. S. Bagnato, and M. F. Andrade, Laser Phys. **18**, 1365 (2008).

12. D. L. Leonard, D. G. Charlton, H. W. Roberts, and M. E. Cohen, J. Esthet. Restor. Dent. **14**, 286 (2002).

13. Y. Nomura, W. Teshima, N. Tanaka, Y. Yoshida, Y. Nahara, and M. Okazaki, J. Biomed. Mater. Res. **63**, 209 (2002).

14. R. W. Mills, A. Uhl, G. B. Blackwell, and K. D. Jandt, Biomater. **23**, 2955 (2002).

15. A. Uhl, R. W. Mills, A. E. Rzanny, and K. D. Jandt, Dent. Mater. **21**, 278 (2005).

16. K. S. Vandewalle, H. W. Roberts, J. L. Andrus, and W. J. Dunn, J. Esthet. Restor. Dent. **17**, 244 (2005).

17. A. N. S. Rastelli, M. F. Andrade, C. Kurachi, and V. S. Bagnato, Rev. Gaücha Odontol. **54**, 139 (2006).

18. D. L. Leonard, J. Esthet. Restor. Dent. **19**, 56 (2007).

19. K. Aravamudhan, C. J. Floyd, D. Rakowski, G. Flaim, S. H. Dickens, F. C. Eichmiller, and P. L. Fan, J. Am. Dent. Assoc. **137**, 213 (2006).

20. M. Dewale, D. Truffier-Boutry, J. Devaux, and G. Leloup, Dent. Mater. **22**, 359 (2006).

21. B. S. Dauvillier, M. P. Aarnts, and A. J. Feilzer, J. Esthet. Dent. **12**, 291 (2000).

22. J. L. Ferracane and J. C. Mitchem, Am. J. Dent. **16**, 239 (2003).

23. J. L. Ferracane, J. R. Condon, B. Pham, and J. C. Mitchem, J. Dent. Res. **78**, 482 (1999).

24. J. Camps, J. Dejou, M. Remusat, and I. About, Dent. Mater. **16**, 432 (2000).

25. M. Brännström, Oper. Dent. **9**, 57 (1984).

26. S. K. Sidhu and L. J. Henderson, Am. J. Dent. **5**, 240 (1992).

27. A. Versluis, D. Tantbirojn, M. R. Pintado, R. DeLong, and W. H. Douglas, Dent. Mater. **20**, 554 (2004).

28. V. Deligeorgi, I. A. Mjör, and N. H. F. Wilson, Primary Dent. Care **8**, 5 (2001).

29. N. Silikas, G. Eliades, and D. C. Watts, Dent Mater. **16**, 292 (2000).

30. A. Peutzfeldt and E. Asmussen, J. Dent. **28**, 447 (2000).

31. R. R. Braga and J. L. Ferracane, J Dent. Res. **81**, 114 (2002).

32. H. Lu, J. W. Stansbury, and C. N. Bowman, Dent. Mater. **20**, 979 (2004).

33. F. C. Calheiros, M. Daronch, F. A. Rueggeberg, and R. R. Braga, Dent. Mater. **24**, 1164 (2008).

34. C. Hansel, G. Leyhausen, U. E. Mai, and W. Geurtsen, J. Dent. Res. **77**, 60 (1998).

35. A. N. S. Rastelli, D. P. Jacomassi, and V. S. Bagnato, Laser Phys. **18**, 1074 (2008).

36. H. Arikawa, T. Kanie, K. Fujii, and N. Shinohara, J. Oral Rehabil. **31**, 74 (2004).

37. H. Jelínková, T. Dostálová, M. Němec, P. Koranda, M. Miyagi, K. Iwai, Y.-W. Shi, and Y. Mansura, Laser Phys. Lett. **4**, 835 (2007).

38. D. A. M. P. Malta, M. A. M. Kreidler, G. E. Villa, M. F. de Andrade, C. R. Fontana, and R. F. Z. Lizarelli, Laser Phys. Lett. **4**, 153 (2007).

39. T. M. Marraccini, L. Bachmann, H. A. Wigdor, J. T. Walsh, Jr., M. L. Turbino, A. Stabholtz, and D. M. Zezell, Laser Phys. Lett. **3**, 96 (2006).

40. T. M. Marraccini, L. Bachmann, H. A. Wigdor, J. T. Walsh, Jr., A. Stabholtz, and D. M. Zezell, Laser Phys. Lett. **2**, 551 (2005).

41. J. R. Condon and J. L. Ferracane, J. Am. Dent. Assoc. **131**, 497 (2000).

42. C. Beznos, Oper. Dent. **26**, 60 (2001).

43. A. D. Loguercio, A. Reis, and R. Y. Ballester, Dent. Mater. **20**, 236 (2004).

44. A. J. Feilzer, L. H. Dooren, A. J. De Gee, and C. L. Davidson, Eur. J. Oral Sci. **103**, 322 (1995).

45. Z. Tarle, A. Knezevic, N. Demali, A. Meniga, J. Sutaloa, G. Unterbrink, M. Ristic, and G. Pichler, Oper. Dent. **31**, 219 (2006).

46. L. G. Cunha, R. C. Alonso, C. S. Pfeifer, L. Correr-Sobrinho, J. L. Ferracane, and M. A. Sinhoreti, J. Dent. **35**, 318 (2007).

47. L. G. Cunha, R. C. Alonso, C. S. Pfeifer, L. Correr-Sobrinho, J. L. Ferracane, and M. A. Sinhoreti, Dent. Mater. **24**, 392 (2008).

48. E. Dall'magro, M. A. Sinhoreti, A. B. Correr, L. Correr-Sobrinho, S. Consani, and R. M. Puppin-Rontani, Braz. Dent. J. **18**, 107 (2007).

49. R. H. Halvorson, R. L. Erickson, and C. L. Davidson, Dent. Mater. **18**, 463 (2002).

50. A. C. Obici, M. A. C. Sinhoreti, M. F. Goes, S. Consani, and L. C. Sobrinho, Oper Dent. **27**, 192 (2002).

51. A. Nalçaci, M. Salbas, and N. Ulusoy, J. Adhes. Dent. **7**, 309 (2005).

52. E. Asmussen and A. Peutzfeldt, Acta Odontol. Scand. **60**, 146 (2002).

53. C. L. Davidson and A. J. De Gee, J. Adhes. Dent. **2**, 167 (2000).

54. M. R. Bouschlicher and F. A. Rueggeberg, J. Esthet. Dent. **12**, 328 (2000).

55. L. G. Cunha, R. C. B. Alonso, A. C. C. Neves, M. F. Góes, J. L. Ferracane, and M. A. C. Sinhoreti, Oper. Dent. **34**, 24 (2009).

56. E. Asmussen and A. Peutzfeldt, J. Dent. Res. **80**, 1570 (2001).

57. A. U. Yap, H. K. Lee, and R. Sabapathy, Dent. Mater. **16**, 172 (2000).

58. A. N. S. Rastelli, D. P. Jacomassi, and V. S. Bagnato, Laser Phys. **18**, 1570 (2008).

59. B. S. Lim, J. L. Ferracane, R. L. Sakaguchi, and J. R. Condon, Dent. Mater. **18**, 436 (2002).

60. C. Charton, P. Colon, and F. Pla, Dent. Mater. **23**, 911 (2007).

61. N. Ilie, K. Felten, K. Trixner, R. Hickel, and E. H. Kunzelmann, Dent. Mater. **21**, 483 (2005).

62. Z. Tarle, A. Meniga, A. Knezevic, J. Sutalo, M. Ristic, and G. Pichler, J. Oral Rehabil. **29**, 662 (2002).

63. E. Asmussen and A. Peutzfeldt, Dent. Mater. **19**, 466 (2003).

64. A. R. Benetti, E. Asmussen, E. C. Munksgaard, M. Dewaele, A. Peutzfeldt, G. Leloup, and J. Devaux, Dent. Mater. (2009, in press).

65. F. Gonçalves, F. C. Calheiros, M. F. Witzel, Y. Kawano, and R. R. Braga, J. Biomed. Mater. Res. B **82**, 89 (2006).

66. L. G. Cunha, R. S. B. Alonso, L. C. Sobrinho, and M. A. C. Sinhoreti, J. Esthet. Restor. Dent. **18**, 29 (2006).

67. R. L. Sakaguchi, B. D. Wiltbank, and C. F. Murchison, Dent. Mater. **20**, 402 (2004).

68. A. Visvanathan, N. Ilie, R. Hickel, and K. H. Kunzel-mann, Dent. Mater. **23**, 777 (2007).

69. M. Tonegawa, G. Yasuda, T. Chikako, Y. Tamura, T. Yoshida, H. Kurokawa, and M. Miyazaki, J. Dent. **37**, 535 (2009).

70. N. Emami, K. J. M. Soderholm, and L. A. Berglund, J. Dent. **31**, 189 (2003).

71. M. F. Witzel, F. C. Calheiros, F. Gonçalves, Y. Kawano, and R. R. Braga, J. Dent. **33**, 773 (2005).

72. J. W. Stansbury and S. H. Dickens, Dent. Mater. **17**, 71 (2001).

73. M. A. Gauthier, I. Stangel, O. H. Ellis, and X. X. Zhu, Biomater. **26**, 6440 (2005).

74. D. Sustercic, P. Cevc, N. Funduk, and M. M. Pintar, J. Mater. Sci. Mater. Med. **8**, 507 (1997).

75. D. R. Morgan, S. Kalachandra, H. K. Shobha, N. Gunduz, and E. O. Stejskal, Biomater. **21**, 1897 (2000).

76. J. M. Antonucci and E. E. Toth, J. Dent. Res. **62**, 121 (1983).

77. S. Imazato, J. F. McCabe, H. Tarumi, A. Ehara, and S. Ebisu, Dent. Mater. **17**, 178 (2001).

78. E. Asmussen, Scand. J. Dent. Res. **92**, 257 (1984).

79. J. L. Ferracane and H. X. Berge, J. Dent. Res. **74**, 1418 (1995).

80. L. G. Lovell, H. Lu, J. E. Elliott, J. W. Stansbury, and C. N. Bowman, Dent. Mater. **17**, 504 (2001).

81. O. Bala, A. Ölmez, and S. Kalayci, J. Oral Rehab. **32**, 134 (2005).

82. P. C. G. Silva, S. T. Porto-Neto, R. F. Z. Lizarelli, and V. S. Bagnato, Laser Phys. Lett. **5**, 220 (2008).

83. K. Fujibayashi, K. Ishimaru, N. Takahashi, and A. Kohno, Dent. Jpn. **34**, 49 (1998).

84. J. L. Ferracane, Crit. Rev. Oral Biol. Med. **6**, 302 (1995).

85. L. E. S. Soares, P. C. S. Liporoni, and A. A. Martin, Oper. Dent. **32**, 160 (2007).

86. A. W. Bennett and D. C. Watts, Dent Mater. **20**, 72 (2004).

87. L. E. Soares, A. A. Martin, A. L. Pinheiro, and M. T. Pacheco, J. Biomed. Opt. **9**, 601 (2004).