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The Effect of Soft-start Polymerization by Second Generation LEDs on the Degree of Conversion of Resin Composite

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Clinical Relevance

Photo-polymerization using second generation LED and halogen light in the soft-start mode of curing was able to produce an adequate degree of conversion in resin composites. The lower degree of conversion produced by low power LED in the soft-start mode could lead to restoration failure, degradation of the organic matrix and recurrent caries.

SUMMARY

Fourier-Transform (FT)—Raman spectroscopy was used to evaluate *in vitro* the degree of conversion (DC) of Charisma dental composite cured by three different light curing units (LCUs) using soft-start and normal protocols. Eighty circular blocks of resin (7 mm in diameter x 2.5 mm thick) were prepared and cured using the following sources: halogen light (Degulux soft-start, n=20, G1-G2), low power light emitting diode (LED) with transparent polymer tip (LD13, n=20, G3-G4) and fiber optic tip (LD13, n=20, G5-G6) and, finally, high power LED (Radii, n=20, G7-G8). The top and bottom surfaces of the blocks were analyzed by FT-Raman spectroscopy. The respective DCs were estimated calculating the peak height ratio of the aliphatic C=C (1640 cm^{-1}) and aromatic C=C (1610 cm^{-1}) Raman modes. The DC at the surfaces ranged between 50% and 60% for the top and 46% and 58% for the bottom. The halogen light and high power LED LCUs with the soft-start and normal protocols produced the highest DC values of dental composite at both surfaces ($p<0.001$). Curing by low power LED in the soft-start protocol did not produce adequate DC at the depth of 2.5 mm. The type of LCU light guide tip did not present a significant statistical difference in the final DC of the dental composite ($p>0.05$).

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INTRODUCTION

Currently, the halogen lamp is the most common light source used for composite photopolymerization in light curing units (LCUs). However, heat generation is the major disadvantage of using the halogen lamp as a light

source.[1-4] Moreover, the bulb, reflector and filter can degrade over time due to high operating temperatures caused by a large quantity of heat, which is produced during cycles. This effect leads to a reduction in curing effectiveness of the light source over time, inadequate physical properties and an increased risk of premature failure of the restorations.[2,5-9]

To overcome inherent problems of the halogen LCU, solid-state light emitting diodes (LEDs) have been purposed for curing light activated dental materials.[2,6-7,10-11] Over the last few years, the LED polymerization of oral biomaterials has become a field of intensive scientific research and has assisted in commercial product development.

A number of studies have addressed the application of blue LED technology to cure dental materials.[1,6] LEDs have an expected lifetime of more than 10,000 hours without significant degradation of light intensity over time.[9] Also, they do not require filters to produce blue light and have low power consumption.[2,10]

Studies have shown that LEDs are potential light sources for replacing conventional halogen lamps in LCUs.[12] LED LCUs with relatively low irradiances are cheap and easily available on the market. However, their use in photopolymerization may result in insufficiently cured composites and, consequently, the inferior mechanical properties of restorations.[12] Another problem that should be pointed out is that light guide tips, which are available for LED LCUs, have a variety of diameters and materials, for example, polymer or fiber optic. The polymer tip scatters the guided light, thus reducing the light intensity at the end of the tip.

On the other hand, high intensity lights may provide higher values of the degree of conversion (DC) and better physical properties, but they also produce higher contraction strain rates during the polymerization process of the composite. This effect increases internal stress and microleakage. An equivalent DC may be achieved by applying lower intensity light for a longer time, or by using variable light intensities over a given time, since the polymerization process depends on total energy rather than on light intensity.[13] Recently, the so called "soft-start" light activation in LCUs has been shown to be an alternative polymerization method. The soft-start protocol has the option of operating with an initial period of low intensity illumination followed by high intensity illumination, which should control stress growth during composite cure.[3,14]

To determine the DC of C=C bonds of the methacrylate group in resin composites, mechanical (dilatometric), calorimetric and spectroscopy techniques can be used.[15] In principle, the latter method provides more reliable results. Spectroscopy methods provide direct measurements of the DC value, because specific vibrational bands can be used as internal standards.[16]

Some molecular vibrational techniques, such as Infrared spectroscopy and Raman spectroscopy, have been used to evaluate the DC produced on dental composites.[14,17-18] Fourier-transform Infrared spectroscopy (FT-IR) has been used to evaluate the DC of dental composites cured by LED and halogen lamp LCUs, detecting the C=C stretching vibrations before and after curing the materials.[2-3,14,19] However, to measure the DC of bulk composite by FT-IR, polymerized samples need to be powdered in a matrix.[20]

Raman spectroscopy has also been used to study the DC of resin composites photo-activated by traditional halogen lamp sources and by argon laser beam. Although this technique is known as non-destructive, it has a high fluorescence signal.[18,21]

While different from the FT-IR technique, no specific sample preparation is required in the Fourier-transform (FT) Raman analysis and, therefore, the measurements are fairly simple and are obtained faster. The FT-Raman technique has been used to evaluate the DC of dental composites produced by LED curing units.[17]

Based on the authors' knowledge, the influence of dental composites produced by the soft-start mode of curing on DC and high power LED LCU has not yet been reported. There are also no reports in the literature regarding the influence of light guide tip material on the DC of dental composites. Thus, this study evaluated the DC in a given composite material by FT-Raman spectroscopy when cured by three different light sources using soft-start and normal protocols: a conventional halogen lamp with optical fiber light guide tip, a high power LED unit and a low power LED with two different light guide tips (polymer and optical fiber).

METHODS AND MATERIALS

A halogen lamp and two LED LCUs in the normal and soft-start mode of operation were used to prepare 80 samples of dental composite. The experimental groups are shown in Table 1.

The dental composite samples were prepared from the universal microhybrid dental composite Charisma (Heraeus Kulzer, Hanau, Germany) shade A3. Each specimen was prepared as follows: 200 mg of uncured composite was placed in a white circular Teflon mold (7 mm in diameter x 2.5 mm thick), compressed, fit to the mold using a condenser and flattened. A mylar strip (Dentart, Polidental, São Paulo, Brazil; dimensions = 10 x 120 x 0.05 mm) was placed over the top of the mold and pressed flat to extrude the excess resin composite.[17]

According to Table 1, the samples were then cured by using one of the following LCUs: (a) the halogen light (Degulux soft-start, Degussa–Hüls AG, Hanau, Germany), (b) the LED 1 unit (LD13, GGDent, Campinas, Brazil) with polymer light guide tip, (c) the

LED 1 unit (LD13) with a fiber optic light guide tip and (d) LED 2 LCU (Radii, SDI Limited, Victoria, Australia). The light intensity of each LCU was measured by means of a radiometer (Field Master GS, Coherent Inc, Auburn, CA, USA). The power density and total energy for each method of light activation were calculated. The technical specifications and measuring results are shown in Table 2.

The curing time recommended by the manufacturer for Charisma dental resin is 20 seconds. The normal mode of each light-curing unit was used as its control (Table 1). The halogen light was used for 20 seconds to cure the G1 and G2 specimens in soft-start and normal protocols, respectively. The soft-start mode was employed for 20 seconds of the 20-second irradiation period. The LD13 unit was used to cure G3, G4, G5 and G6 specimens. The soft-start protocol was employed for 10 seconds of the 20-second irradiation period for the LD13 unit in G3 and G5 specimens. The normal protocol was employed for 20 seconds of the LD13 unit in the G4 and G6 specimens. The soft-start mode was employed for five seconds of the 25 second-irradiation period for the Radii unit in G7 specimens. The Radii unit cured the G8 specimens group for 25 seconds in normal mode.

Towards the end of specimen preparation, the dental composite specimens were stored in the dark for 24 hours.[10]

Table 1: *Division of Experimental Groups*

Group	Light Curing Unit	Light Curing Mode
G1	Halogen lamp (Degulux soft-start)	Soft-start
G2	Halogen lamp (Degulux soft-start)	Normal
G3	LED 1 (LD13–polymer tip)	Soft-start
G4	LED 1 (LD13–polymer tip)	Normal
G5	LED 1 (LD13–optical fiber tip)	Soft-start
G6	LED 1 (LD13–optical fiber tip)	Normal
G7	LED 2 (Radii)	Soft-start
G8	LED 2 (Radii)	Normal

Table 2: *Technical Specifications of the Light Curing Units Used to Prepare the Dental Composite Specimens*

Parameters	G1 and G2	G3 and G4	G5 and G6	G7 and G8
Power density (mW/cm^2)	420/745	45/140	40/130	600/800
Wavelength (nm)	400-500	470	470	460
Tip diameter (mm)	8	8	8	8
Total time of curing (seconds)	20	20	20	25
Time of light in reduced irradiance (seconds)	20	10	10	5
Total energy density (J/cm^2)	8.36/14.73	0.87/2.78	0.795/2.56	14.93/19.90

The top and bottom surfaces were analyzed by FT-Raman spectroscopy in order to evaluate the DC. The spectra of the uncured and cured resins were obtained by an FT-Raman Spectrometer (RFS 100/S, Bruker Inc, Karlsruhe, Germany) using 100 scans. The spectrum resolution was set to 4 cm^{-1}. The samples were excited by the defocused line of an Nd:YAG laser source at λ=1064.1 nm with maximum laser power of approximately 90 mW at the sample.

The uncured resin was positioned on an aluminum rod in a sample holder mounted on an optical rail for spectrum collection. For the 80 cured specimens, three spectra of the top surface and another three spectra of the bottom surface were collected, resulting in a total of 480 spectra. Based on the measurements, one average spectra for each surface was obtained, ensuing in 160 spectra.

The average FT-Raman spectra were analyzed by selecting a range between 1590 and 1660 cm^{-1}. The Raman peaks corresponding to the vibrational stretching modes at 1610 and 1640 cm^{-1} were fitted in Gaussian shapes to obtain the height of the peaks by Microcal Origin software (Microcal Software Inc, Northampton, MA, USA).

A comparison of the height ratio of the aliphatic carbon-carbon double bond (C=C) at 1640 cm^{-1} with that of the aromatic component at 1610 cm^{-1} for the cured and uncured conditions was performed in order to estimate the DC using the equation (1). The aromatic C=C peak at 1610 cm^{-1} originated from the aromatic bonds of the benzene rings in the monomer molecules, and its intensity remains unchanged during the polymerization reaction. The percentage of DC is then calculated by:

$$DC\ (\%) = 100*[1 - R] \qquad (1)$$

where R = the percentage of uncured resin that is determined by band height at 1640cm^{-1}/ band height at 1610cm^{-1}.[14,22-23]

The mean value and standard deviation of the DC were calculated for each series. The DC obtained in the specific soft-start protocol was compared to the data generated by using the respective LCU without the soft-start protocol (in the normal mode).

The FT-Raman results were statistically analyzed by one-way ANOVA at a 95% confidence level. The Kolmorogov and Smirnov tests verified the normal distribution of the sample data. The standard deviations were tested by Bartlet statistics. The Tukey-Kramer multi com-

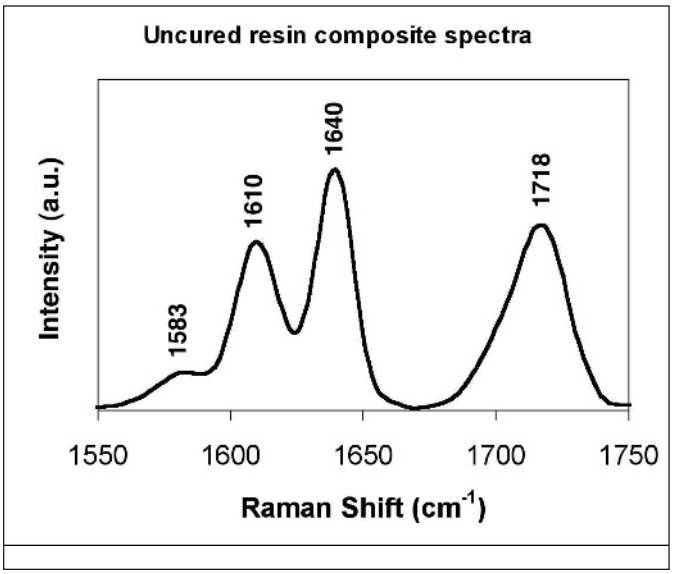

Figure 1. *FT-Raman spectra of uncured Charisma dental composite showing the C=C aromatic, C=C and C=O vibrational bands at 1583, 1610, 1640 and 1718 cm^{-1}.*

parisons post-hoc test was also performed to test the significance of DC between the experimental groups. All statistical analyses were performed by Instat software (GraphPad Software, San Diego, CA, USA).

RESULTS

Figure 1 shows the FT-Raman spectrum of uncured resin. The main vibrational modes have been previously identified and are assigned to the C=C stretching mode of the aromatic group at 1583 and 1610 cm^{-1}, the Methacrylate C=C stretching mode at 1640 cm^{-1} and the C=O stretching mode at 1718 cm^{-1}.[17]

The calculated DC (by the Equation 1) on the dental composite Charisma ranged from 46 ± 2.0 to 60 ± 1.1% for the bottom and top surfaces, respectively. The DC values calculated for the groups are shown in the Table 3. The highest DC values for top and bottom surfaces were found in the G7 and G8 specimens.

The capital letters featured in columns two and three of Table 3 show the statistical comparisons of the DC produced between the top and bottom surfaces of each group. Very low DC values were obtained for the bottom surface of the G3 and G5 specimens (p<0.001). Significantly higher DC values were obtained for the top surface of the G2 specimens (p<0.05). For the G1, G4, G6, G7 and G8 specimens, no statistically significant differences were observed between the top and bottom surfaces (p>0.05).

Statistical comparisons among the LCU groups for normal and soft-start protocols on the top and bottom surfaces are shown in small letters in Table 3. No significant statistical differences were observed for the top surface between the G1-G2 and G7-G8 specimens

Table 3: *Mean and Standard Deviation (SD) of the Degree of Conversion (%) Measured at the Top (t) and Bottom (b) Surfaces from Dental Composite of the Experimental Groups (n=10)*

Groups	DC% (top) SD	DC% (bottom) SD
G1	56 ± 1.8$^{a\ A}$	55 ± 3.2$^{a\ A}$
G2	58 ± 1.3$^{a\ A}$	55 ± 0.9$^{a\ B}$
G3	50 ± 1.6$^{b\ A}$	46 ± 2.0$^{b\ B}$
G4	53 ± 1.1$^{c\ A}$	51 ± 2.3$^{c\ A}$
G5	52 ± 1.6$^{bd\ A}$	47 ± 2.1$^{bd\ B}$
G6	54 ± 2.6 $^{ce\ A}$	52 ± 2.9$^{ce\ A}$
G7	60 ± 1.1$^{f\ A}$	58 ± 1.3$^{f\ A}$
G8	59 ± 1.5 ^{A}	57 ± 0.9$^{f\ A}$

Means followed by the same small letter in the column and capital letter in the row indicate no statistical differences at p=0.05.

(p>0.05). However, in the G4 and G6 specimens, the DC was statistically higher than in the G3 and G5 specimens (p<0.05).

At the bottom surface, the same statistical differences were observed between the G1-G2 and the G7-G8 specimens. In the G4 and G6 specimens, the DCs were lower than in the G3-G5 specimens with statistical difference (p<0.001). At the top and bottom surfaces, non-significant statistical differences were observed between the G3-G5 specimens and the G4-G6 specimens (p>0.05)

DISCUSSION

A higher DC, which is primarily related to curing light intensity and exposure time, conflicts with the objective of achieving optimal marginal integrity, because of increased contraction.[3] To minimize shrinkage stress, "soft cure" or "soft-start" LCUs were developed. These LCUs have the option of operating with an initial period of low intensity illumination, which should reduce stress development during composite curing.[3,14] However, soft-start polymerization systems have demonstrated no significant reduction in polymerization shrinkage, no differences in hardness and no better marginal adaptation of resin composite restorations bonded to dentinal cavities.[24]

In this study, FT-Raman spectroscopy was used to evaluate a possible interference in the DC of resin composites produced by the type of LCUs, by light irradiance, by soft-start mode and by LCU light guide tip.

In a previous study, Pianelli and others reported that the DC (gel point) of Z100 dental composite measured by Raman spectroscopy was close to 50% when cured for 40 seconds by a halogen lamp.[22] In this study, the DC of Charisma dental resin cured by halogen lamp in soft-start and normal modes was 56% and 58%, respectively, at the top surface. This result can be explained, because DC would vary to a given composite due to its unique combination of filler, resin characteristics and

formulation.[25] This difference in DC is also probably due to differences in light permeability to filler, monomer composition and type, concentration of the initiator, inhibitor and accelerator in composite materials. The ratio of filler relative to resin is also important, since penetration of light into the composite is more difficult as the proportion of filler is higher.[2]

Several studies reported that the DC of resin composite produced by the halogen lamp was higher than that produced by LED LCUs due to higher light intensities.[3,8] Similar results on DC produced by a halogen LCU with a light intensity of 600 mW/cm^2 and an LED with a light intensity of 12 mW/cm^2 was found by Knezevic and others.[19] Other studies reported that LED LCU cured better than did the halogen light.[1,6] However, those studies did not investigate DC in the soft-start mode produced by high powered LED LCUs.

In this study, DC produced by conventional halogen light and by high power LED (Radii) between the soft-start and normal protocols of each light source did not show a significant statistical difference for both surfaces ($p>0.05$). However, polymerization produced by low power LED (LD13) in the soft-start mode with polymer and optical fiber light guide tips produced the lowest DC at the bottom surface with a significant statistical difference ($p<0.001$) from the normal protocol.

In this case, the calculated DC of 46% and 47% for G3 and G5 specimens showed that lower irradiance of LED 1 in the soft-start mode produced inadequate polymerization at the composite bottom surface.

Comparisons of DC between normal and soft-start protocols of each LCU at the same surface showed significant statistical differences when the low power LED was used ($p<0.05$–top; $p<0.001$–bottom). However, it was verified that, low irradiance in the first 10 seconds (40-45 mW/cm^2) of the soft-start mode, added to low power of the LED 1 (130-140 mW/cm^2), affects the efficiency of the LCU in composite polymerization.

The influence of light guide tip material on DC was not statistically significant ($p>0.05$) between the polymer (G3-G5) and fiber optic tip (G4-G6) specimens cured in soft-start and normal protocols, respectively. However, the normal protocol produced higher DC values on resin composite.

To date, the minimum DC for a clinically satisfactory restoration has not been precisely established. Nevertheless, 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.[14]

In this study, composite polymerization by low power LED in the soft-start protocol produced a DC below 53% at the top surface (50%–G3; 52%–G5) and below 48% at the bottom surface (46%–G3; 47%–G5), with possible influence on composite physical properties. However, in a normal protocol, a DC below 55% at the top surface (53%–G4; 54%–G6) and a DC below 53% at the bottom surface (51%–G4; 52%–G6) was found.

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.[26]

Therefore, this fact could directly effect biocompatibility of the composite restoration,[21] since increasing the DC number of methacrylate pendant groups available for hydrolytic degradation decreases.[26] Hydrolytic degradation and oxidation of composites may lead to the leaching of different degradation products from resin composite. 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.[26]

From the FT-Raman spectra, a direct influence of the power density of LCUs on the DC of composite has been verified. The soft-start mode of polymerization of low power LED proved to be unnecessary, because lower irradiance produced at the first 10 seconds of polymerization reduced the total irradiance available to polymerization. The soft-start protocol did not influence the DC in high power LED and halogen light cured specimens.

High power LED and halogen light LCUs in both modes of polymerization produced a higher composite DC. 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 hours, 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.[4-5]

FT-Raman spectroscopy was shown to be an adequate tool to measure the DC of dental composites. The measurements are fairly simple, since no specific sample preparation or conditions are required. Raman measurements can be carried out in normal atmospheric conditions without the need for a high vacuum. Finally, since this technique is non-destructive, samples can be used in multiple analyses.

CONCLUSIONS

The authors have shown that halogen light and high power LED LCUs in soft-start and normal mode of polymerization produced higher DC values of dental composites than other LCUs. Polymerization by low power LED LCU in the soft-start protocol did not produce an

adequate DC at the depth of 2.5 mm in dental composite. The type of light guide tip material did not present a significant statistical difference on the final DC of dental composite.

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References

1. Fujibayashi K, Ishimaru K, Takahashi N & Kohno A (1998) Newly developed curing unit using blue light-emitting diodes *Dentistry Japan* **34** 49-53.
2. Yoon TH, Lee YK, Lim BS & Kim CW (2002) Degree of polymerization of resin composites by different light sources *Journal of Oral Rehabilitation* **29(12)** 1165-1173.
3. Tarle Z, Meniga A, Knezevic A, Sutalo J, Ristic M & Pichler G (2002) Composite conversion and temperature rise using a conventional, plasma arc, and an experimental blue LED curing unit *Journal of Oral Rehabilitation* **29(7)** 662-667.
4. Nitta K (2005) Effect of light guide tip diameter of LED-light curing unit on polymerization of light-cured composites *Dental Materials* **21(3)** 217-223.
5. Bennett AW & Watts DC (2004) Performance of two blue light-emitting-diode dental light curing units with distance and irradiation-time *Dental Materials* **20(1)** 72-79.
6. Mills RW, Uhl A, Blackwell GB & Jandt KD (2002) High power light emitting diode (LED) arrays versus halogen light polymerization of oral biomaterials: Barcol hardness, compressive strength and radiometric properties *Biomaterials* **23(14)** 2955-2963.
7. Kurachi C, Tuboy AM, Magalhães DV & Bagnato VS (2001) Hardness evaluation of a dental composite polymerized with experimental LED-based devices *Dental Materials* **17(4)** 309-315.
8. Jandt KD, Mills RW, Blackwell GB & Ashworth SH (2000) Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs) *Dental Materials* **16(1)** 41-47.
9. Stahl F, Ashworth SH, Jandt KD & Mills RW (2000) Light-emitting diode (LED) polymerization of dental composites: Flexural properties and polymerization potential *Biomaterials* **21(13)** 1379-1385.
10. Dunn WJ & Bush AC (2002) A comparison of polymerization by light-emitting diode and halogen-based light-curing units *Journal of the American Dental Association* **133(3)** 335-341.
11. Mills RW, Jandt KD & Ashworth SH (1999) Dental composite depth of cure with halogen and blue light emitting diode technology *British Dental Journal* **186(8)** 388-391.
12. Uhl A, Michaelis C, Mills RW & Jandt KD (2004) The influence of storage and indenter load on the Knoop hardness of dental composites polymerized with LED and halogen technologies *Dental Materials* **20(1)** 21-28.
13. Sakaguchi RL & Berge HX (1998) Reduced light energy density decreases post-gel contraction while maintaining degree of conversion in composites *Journal of Dentistry* **26(8)** 695-700.
14. Silikas N, Eliades G & Watts DC (2000) Light intensity effects on resin-composite degree of conversion and shrinkage strain *Dental Materials* **16(4)** 292-296.
15. Sandner B, Kammer S & Wartewig S (1996) Crosslinking copolymerization of epoxy methacrylates as studied by Fourier transform Raman spectroscopy *Polymer* **37(21)** 4705-4712.
16. De Santis A & Baldi M (2004) Photo-polymerisation of composite resins measured by micro-Raman spectroscopy *Polymer* **45(11)** 3797-3804.
17. Soares LES, Rocha R, Martin AA, Pinheiro ALB & Zampieri M (2005) Monomer conversion of composite dental resins photoactivated by a halogen lamp and a LED: An FT-Raman spectroscopy study *Quimica Nova* **28(2)** 229-232.
18. Soares LES, Martin AA & Pinheiro ALB (2003) Degree of conversion of composite resin: A Raman study *Journal of Clinical Laser Medicine and Surgery* **21(6)** 357-362.
19. Knezevic A, Tarle Z, Meniga A, Sutalo J, Pichler G & Ristic M (2001) Degree of conversion and temperature rise during polymerization of composite resin samples with blue diodes *Journal of Oral Rehabilitation* **28(6)** 586-591.
20. Imazato S, McCabe JF, Tarumi H, Ehara A & Ebisu S (2001) Degree of conversion measured by DTA and FTIR *Dental Materials* **17(2)** 178-183.
21. Soares LE, Martin AA, Pinheiro AL & Pacheco MT (2004) Vicker's hardness and Raman spectroscopy evaluation of a dental composite cured by an argon laser and a halogen lamp *Journal of Biomedical Optics* **9(3)** 601-608.
22. Pianelli C, Devaux J, Bebelman S & Leloup G (1999) The micro-Raman Spectroscopy, a useful tool to determine the degree of conversion of light-activated composite resins *Journal of Biomedical Materials Research (Applied Biometry)* **48(5)** 675-681.
23. Xu J, Butler IS, Gibson DF & Stangel I (1997) High-pressure infrared and FT-Raman investigation of a dental composite *Biomaterials* **18(24)** 1653-1657.
24. Micali B & Basting RT (2004) Effectiveness of composite resin polymerization using light-emitting diodes (LEDs) or halogen-based light-curing units *Pesquisa Odontológica Brasileira* **18(3)** 266-270.
25. Bala O, Ölmez A & Kalayci S (2005) Effect of LED and halogen light curing on polymerization of resin-based composites *Journal of Oral Rehabilitation* **32(2)** 134-140.
26. Yap AU, Lee HK & Sabapathy R (2000) Release of methacrylic acid from dental composites *Dental Materials* **16(3)** 172-179.