Quantification of Polymerization Using Er:YAG Laser Ablation Techniques

Denis P. Jacomassi[a], Alessandra Nara S. Rastelli[b], Vanderlei S. Bagnato[c]

[a] Physicist, PhD student, Physics Institute of São Carlos, University of São Paulo, SP, Brazil.
[b] Researcher in Lasers and Dental Materials, Physics Institute of São Carlos, University of São Paulo, SP, Brazil.
[c] Titular Professor, Physics Institute of São Carlos, University of São Paulo, SP, Brazil.

Purpose: The aim of this study was to evaluate the efficacy of polymerization of composite resin photocured with different wavelengths and irradiation times by means of ablation techniques with Er:YAG laser.

Materials and Methods: A microhybrid composite resin was photocured with argon laser (Coherent, Innova 200-20) at 400 mW/cm^2 for 15, 40, 60, 300, and 900 s. The wavelengths used were 476.5, 488.0, 502.7, and 514.5 nm. The samples were ablated with Er:YAG laser at three energy levels (100, 200, and 300 mJ), a fixed frequency of 2 Hz, and water flow of 0.12 ml/s for 10 s. The ablated volume was measured to quantify polymerization. Two-way ANOVA and Tukey's test were used to analyze the data.

Results: The results showed a more effective polymerization for the wavelength of 476.5 nm with low irradiation times (15, 40 and 60 s). Longer photoactivation (300 and 900 s) and a wavelength of 488.0 nm resulted in less ablation.

Conclusion: The ablation techniques with Er:YAG laser can be used for evaluation of efficacy of polymerization of the composite resin and showed that the wavelengths of 476.5 and 488.0 nm provided the best polymerization rate.

Keywords: photocuring, composite resins, argon laser, Er:YAG, ablation rate.

Composite resins have become very popular restoration materials due mainly to good operator control of contouring and color combination, immediately resulting in satisfactory shape, function, and durability. However, the color of composite resin changes with time, depending on the dental structure.[1,2] In addition, some composite resins present insufficient properties due to inadequate polymerization, fracture, greater solubility in the oral environment, recurrent caries, increase of microleakage, and pulp irritation.[3]

This makes it necessary to replace the unsatisfactory restorations. The ablation technique is a good option for removing composite resins, because it provides greater patient comfort due to absence of vibration and heating.[3] The Er:YAG laser operating at pulse durations in the microsecond range is established as a suitable instrument for selective and precise photomechanical removal of carious dental tissue and restorative materials.[4,5]

The Er:YAG laser has a wavelength of 2.94 µm. It is resonant with the water molecule vibration present in the tissue or materials. The fast heating of these water molecules rapidly transforms the liquid phase to vapor, generating internal pressures and microexplosions of material.[4,5]

Some studies have shown that ablation rate changes for different composite resins and conditions of photocuring.[6,7] Laser ablation easily removes undesired

material while conserving the remaining dental tissue because of the difference in threshold energy between composite resin and dental tissue necessary to start ablation.

Several methods are commonly used to evaluate the photocuring efficacy or the polymerization rate of composite resins, such as mechanical or degree of conversion tests.[8-10] The laser ablation technique can also be used to evaluate the photocuring efficacy.[4,7] Ablation is different for each material, and the ablated volume is related to the difficulty of ablation, or resistance of the material. Lizarelli described the quality of light curing for different power densities.[7] However, other studies are necessary to verify the sensitivity and when this technique can be used. The absorption spectrum of camphorquinone, the most popular photosensitizer for commercial, visible light-cured resins, has a peak value at 470 nm. Camphorquinone is thus very sensitive to light in the blue region of the visible light spectrum.

The use of argon laser to investigate the influence of the wavelength on the polymerization process has been the best option for this evaluation. Low beam divergence of the laser radiation is an added advantage.[11] Besides, some studies suggest that argon laser curing results in superior characteristics of cured composite because it generates a narrower bandwidth.[12] Curing with argon laser also resulted in lower in vitro temperature increases in the composite resin.[13,14]

The polymerization process is affected by the particular chemical composition of the composite resin, color, amount of fillers, particle size of the fillers; in addition, many factors related to the light-curing units also affect the polymerization process, including light intensity or power density, power, wavelength, and irradiation times.[15]

Thus, the purpose of this study was to employ the ablation technique to evaluate the quality of photoactivation of a microhybrid composite resin using different wavelengths and irradiation times.

MATERIALS AND METHODS

Resin and laser

The microhybrid composite resin Filtek Z-250 (batch no. 1370, 3M/ESPE; St. Paul, MN, USA) shade A2 was used to create the sample for this study. The material is based on a bisphenol glycidyl methacrylate (bis-GMA) / urethane dimethacrylate (UDMA)/bisphenol ethylene methacrylate (bis-EMA) resin matrix, with camphorquinone as photoinitiator and 60 vol% inorganic filler content (particle size 0.19 to 3.3 microns). The inorganic filler is based on zirconia/silica. This material, Filtek Z-250, is clinically indicated as a universal hybrid composite resin for anterior and posterior restorations.

The argon laser (Coherent, Innova 200-20, serial number 3240, USA) was used as the light-curing unit (LCU), operated in continuous mode (CW), and can be adjusted for the multiline or single-line modes.

A lens set was used with a focal length around 3.0 cm to maintain a beam of Gaussian profile.[7] The laser beam was approximately 0.8 cm.

Sample preparation

The composite resin samples (n = 60) were made in a metallic mould with standardized dimensions with 8.0 mm diameter and 2.0 mm thickness, where the composite resin was packed in a single increment. The top surface was covered with a mylar strip during the polymerization process. A glass sheet with 1 mm thickness was positioned, and a 1-kg weight was used to pack the composite resin and to standardize the thickness of the samples.

The composite resin samples were photoactivated with argon laser at the wavelengths of 476.5, 488.0, 501.7, and 514.5 nm, all at a standardized power density of 400 mW/cm^2. The samples were photoactivated for 15, 40, 60, 300, and 900 s. Figure 1 shows the photoactivation procedure with argon laser.

Ablation rate

After the polymerization process, the samples were stored dry at 37°C for 24 h. The laser used in this evaluation was the Er:YAG laser system (Twin Light, Fotona Medical Lasers; Ljubljana, Slovenia, serial number 99000374) operating in the microsecond regime with pulse duration between 200 and 450 μs, emitting at a 2.94 μm wavelength, maximum energy per pulse of 500 mJ, repetition rate or pulse frequency of 2 to 15 Hz. This laser bears an articulated arm, a handpiece with a sapphire window operating through a noncontact beam with a focused transversal section area of about 0.0038 x cm^2 and an air/water spray cooling system.

The experimental set-up ensured that the laser beam was applied perpendicular to the sample surface and positioned at a focal distance of 12.0 ± 1.0 mm (Fig 2).
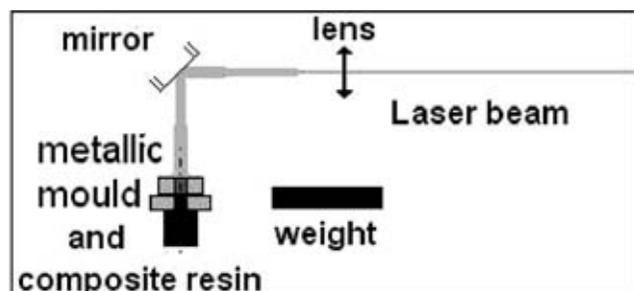
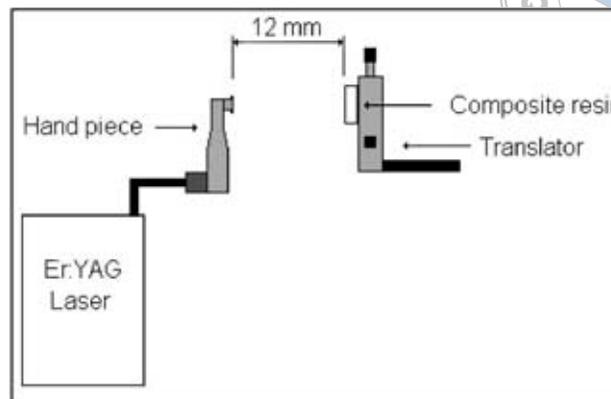**Fig 1** Set up for photo-activation procedure with argon laser.

Fig 2 Experimental set-up.

Each sample was ablated with the Er:YAG laser at the given focal length, while varying the energy per pulse (100, 200 and 300 mJ) with a fixed repetition rate of 2 Hz, water flow of 0.12 ml/s, for 10 s. Nine (n = 9) microcavities were made for each sample. The total number of microcavities was 540 (4 wavelengths x 5 exposure times x 3 energy densities x 9 microcavities = 540 holes).

The diameter and depth measurements were made using an optical microscope (40X magnification), followed by calculating the volume of removed material assuming a conical shape of the resultant microcavity.[7] The following formula was used to calculate the ablated material volume:

$$V = \frac{\pi \times D^2 \times P}{12}$$

where D = the microcavity diameter and P = the depth.

Results were statistically analyzed using two-way ANOVA and Tukey's test (p < 0.05).

RESULTS AND DISCUSSION

Table 1 shows the two-way ANOVA for the measured ablation rate values for different wavelengths and irradiation times.

The results are shown in Figs 3 to 7. The values were expressed in a volume graph (mm³) as a function of energy per pulse (mJ), with each figure presenting one photocuring exposure time. All samples were ablated with Er:YAG laser for 10 s at a fixed frequency of 2 Hz.

Adequate photoactivation is an important factor for obtaining successful restorations and good clinical performance of resin restorative materials. Otherwise, the quality of the restoration and satisfaction of the patients will not be good. Hence it is important to correctly evaluate the polymerization of composite resins. The ablation rate is an additional method for evaluating photoactivation efficacy, as already used by Lizarelli[7] to evaluate the effect of different light intensities or power densities and irradiation times on the photoactivation procedure.

The lower volume removed in the ablation process is attributed to the greater difficulty in removing the composite resin. This can be explained by the higher bond energy or intermolecular forces between the polymer chains, crosslinks and bond between chains and inorganic fillers. In this study, this phenomenon is termed ablation resistance.

In resinous materials, the quantities of the crosslinks and residual monomer change as a function of photoactivation parameters. The quantities of the crosslinks are a co-determinant of the mechanical properties of the resulting polymer.[15] Optimal polymerization increases the crosslinks and consequently ablation resistance.

The mechanical and physical properties of composite resins are frequently correlated with the absorption spectrum of the photoinitiator. The photoinitiator in this study was camphorquinone, which has an absorption spectrum between 400 and 520 nm, with a maximum peak around 470 nm. In theory, the the highest

Table 1 ANOVA test results

	ANOVA: Original values				
Variance factors	Square Sum	Degrees of freedom	Square average	F	P
Wavelengths E=100 mJ; 15 s	0.0001641	3	0.0000547	11.72	0.0002
Wavelengths E=200 mJ; 15 s	0.0095056	3	0.0031685	61.43	0.0000
Wavelengths E=300 mJ; 15 s	0.016347	3	0.005449	37.42	0.0000
Wavelengths E=100 mJ; 40 s	0.0002321	3	0.0000774	17.22	0.0000
Wavelengths E=200 mJ; 40 s	0.0031067	3	0.0010356	14.25	0.0000
Wavelengths E=300 mJ; 40 s	0.010892	3	0.003631	25.86	0.0000
Wavelengths E=100 mJ; 60 s	0.0001891	3	0.0000630	7.79	0.0000
Wavelengths E=200 mJ; 60 s	0.0067572	3	0.0022524	64.79	0.0000
Wavelengths E=300 mJ; 60 s	0.017893	3	0.005964	29.23	0.0000
Wavelengths E=100 mJ; 300 s	0.0002136	3	0.0000712	8.60	0.0000
Wavelengths E=200 mJ; 300 s	0.0063090	3	0.0021030	46.90	0.0000
Wavelengths E=300 mJ; 300 s	0.0125294	3	0.0041765	58.19	0.0000
Wavelengths E=100 mJ; 900 s	0.0002904	3	0.0000968	40.71	0.0000
Wavelengths E=200 mJ; 900 s	0.0067065	3	0.0022355	41.11	0.0000
Wavelengths E=300 mJ; 900 s	0.002182	3	0.000727	4.36	0.0110

ablation resistence will result for the wavelengths closest to the absorption peak of the photoinitiator.

Figure 3 displays the volume-energy per pulse relation when the composite resin was photocured for 15 s with the four different wavelengths. It was clear that when the low energy per pulse (100 mJ) was used for the all wavelengths, the volumes removed were equivalent and the difference was not significant. At medium energy per pulse (200 mJ), a higher volume was removed with the wavelength of 514.5 nm. A lower volume was removed for the wavelength of 476.5 nm. At high energy per pulse (300 mJ), a greater volume was removed with the wavelength 514.5 nm, and a lesser volume was removed with 488.0 nm. Comparing the curves for the ablated volume of the photocured samples with wavelengths of 476.5 and 488.0 nm reveals modified curve profiles. For the wavelength of 476.5 nm, the profile of the curve is similar to other wavelengths. For the wavelength of 488.0 nm, the profile of the curve is modified between 200 and 300 mJ, resulting in less ablated volume for the energy of 300 mJ.

A similar result was observed in a different study which evaluated the efficiency of polymerization for different irradiation times.[7] It was explained by the plume-shielding effect. This phenomenon can be described as a plume of ablated material that is interposed between the target material and incident laser beam. This plume shielding impairs both water penetration in the material and the laser beam; the lack of water decreases the ablation efficacy and thus the vol-

Fig 3 Volume graph (mm³) as a function of energy per pulse for composite resin photoactivated for 15 s and ablated with Er:YAG laser (2.94 μm and frequency fixed at 2 Hz for 10 s).

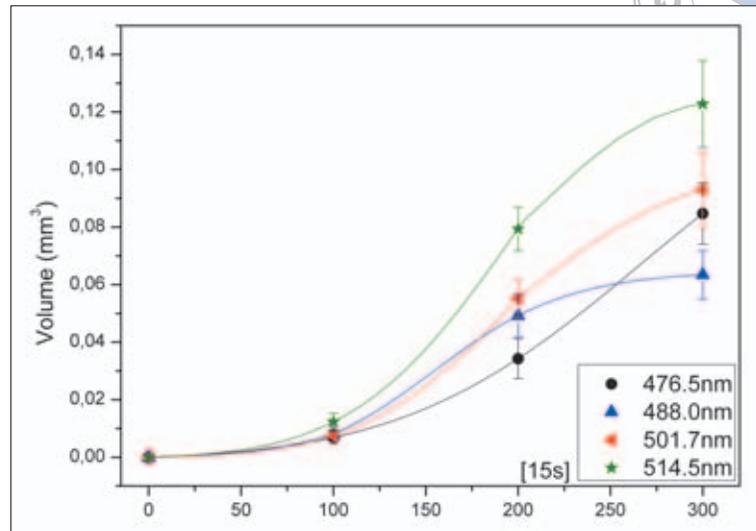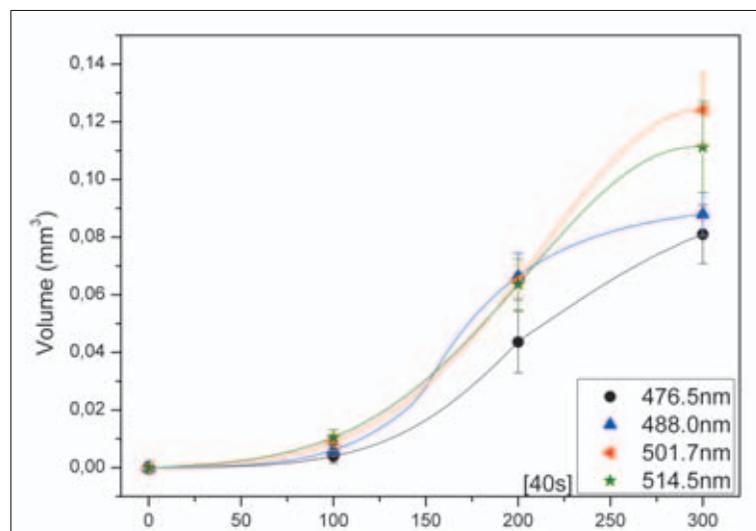**Fig 4** Volume graph (mm³) as a function of energy per pulse for composite resin photoactivated for 40 s and ablated with Er:YAG laser (2.94 μm and frequency fixed at 2 Hz for 10 s).

ume of material removed. This phenomenon occurs at high energy per pulse; at low energies, the plume and shielding effect are negligible. With high energy at the start of ablation, the amount of material removed and ejected is great. However, the shielding-plume effect quickly decreases ablation efficiency. This phenomenon occurs for all wavelengths, though with different intensities.

When evaluating photocuring efficacy with the ablation rate method, it must be verified whether another mechanism – such as the plume shield – may decrease the ablation efficiency; otherwise the results may be incorrectly interpreted.

To facilitate interpretation, it must be considered that at 200 mJ, the shielding-plume effect is negligible,

and at 300 mJ the effect is not negligible and occurs with different intensity. Other experiments are necessary to find the reason for this difference. The photopolymerization results agree with the microhardness test as described by Namoto.[16]

Figure 3 shows that greatest ablation resistance occurred for the wavelength of 476.5 nm. The second and third highest ablation resistance was observed for 488.0 and 501.7 nm, however, the difference was not significant. The lowest ablation resistance was observed for wavelength 514.5 nm. This fact can be explained by the camphorquinone spectrum absorption.

Figure 4 displays the volume-energy per pulse relation when the composite resin was photocured for 40 s for all wavelengths. Here, too, the greatest ablation
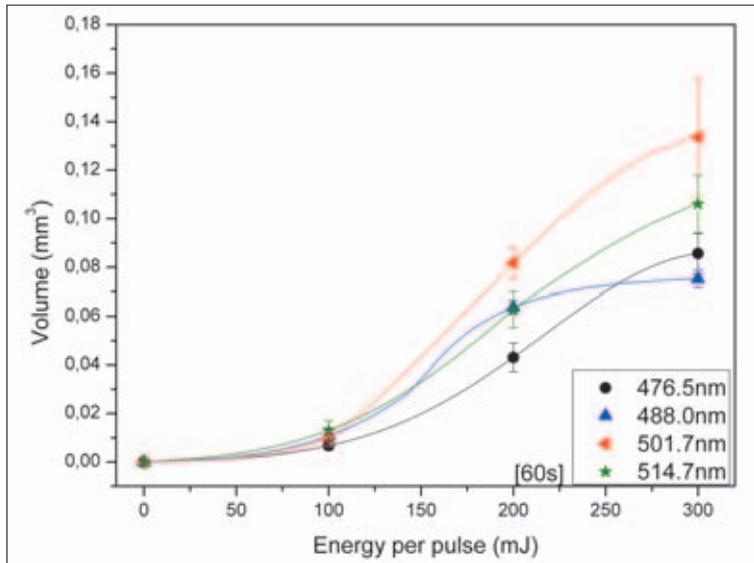
Fig 5 Volume graph (mm³) as a function of energy per pulse for composite resin photoactivated for 60 s and ablated with Er:YAG laser (2.94 µm and frequency fixed at 2 Hz for 10 s).
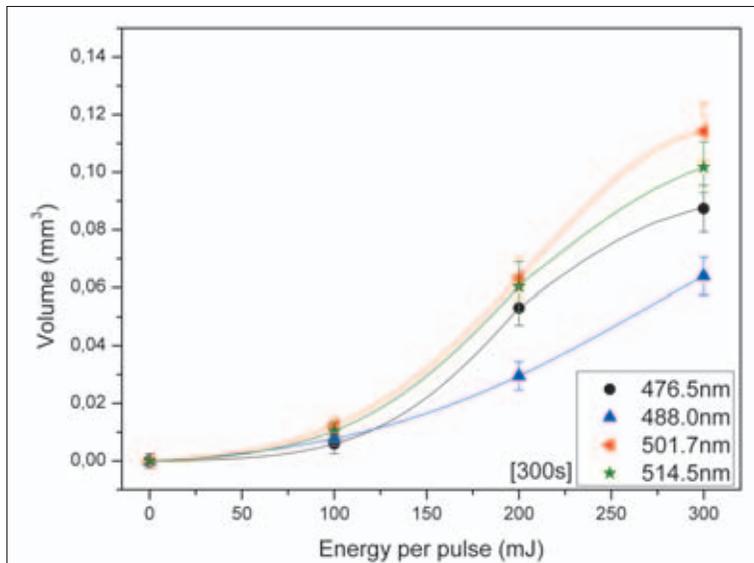

Fig 6 Volume graph (mm³) as a function of energy per pulse for composite resin photoactivated for 300 s and ablated with Er:YAG laser (2.94 µm and frequency fixed at 2 Hz for 10 s).

Fig 7 Volume graph (mm³) as a function of energy per pulse for composite resin photoactivated for 900 s and ablated with Er:YAG laser (2.94 µm and frequency fixed at 2 Hz for 10 s).
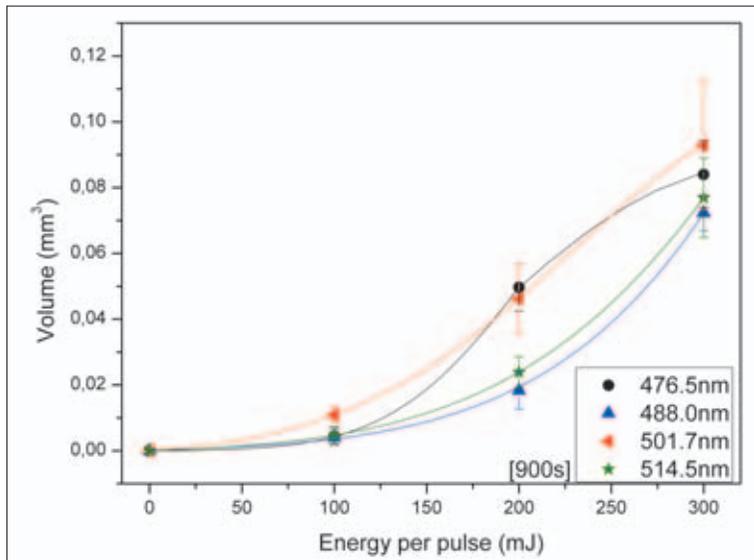
resistance occurred for 476.5 nm, but the other wavelengths did not present significant differences.

Figure 5 shows the volume-energy per pulse relation when the composite resin was photocured for 60 s. It was shown that the highest ablation resistance also occurred for 476.5 nm. The ablation resistence was similar for the wavelengths of 488.0 and 514.5 nm, and the lowest ablation resistance was for 501.7 nm.

Photoactivation with argon laser is rapid, necessitating a short irradiation time.[17-19] The high exposure times of this study are not used in clinical situations; therefore, there are no clinical studies of photoactivation and ablation with such high irradiation times.

Figures 6 and 7 show the volume-energy per pulse relation when the composite resin was photocured for 300 and 900 s. It was shown that the highest ablation resistance also occurred for 488.0 nm. Theoretically, the highest value would occur for the wavelength of 476 nm. There could be two explanations for this: The first is the embrittlement of material due to a temperature rise, and the second the difference of photodegradation of photoinitiator for the two wavelengths. It is clear that to test either of these hypotheses further studies are required.

CONCLUSIONS

Different wavelengths and photoactivation times influenced the removed volume during the ablation process. The removed volumes differed as a function of the irradiation time and wavelength for photoactivation, as shown by our results. Such differences can be used to evaluate the photocuring of the composite resin. For shorter photoactivation times, the best wavelengths for polymerization were 476.5 and 488.0 nm, depending on the energy used for ablation. For longer irradiation times, the optimum wavelength for polymerization was 488.0 nm.

ACKNOWLEDGMENTS

REFERENCES

1. Lee YK, Lim BS, Powers JM. Color changes of dental resin composites by a salivary enzyme. J Biomed Mater Res B Appl Biomater 2004;70:66-72.

2. Janda R, Roulet JF, Kaminsky M, Steffin G, Latta M. Color stability of resin matrix restorative materials as a function of the method of light activation. Eur J Oral Sci 2004;112:280-285.

3. Martin FE, A survey of the efficiency of visible light curing units. J Dent 1998;26:239-243.

4. Lizarelli RFZ, Kurachi C, Misoguti L, Bagnato VS. Characterization of enamel and dentin response to Nd:YAG picosecond laser ablation. J Clin Laser Med Surg 1999;17:127-131.

5. Lizarelli RFZ, Moriyama LT, Bagnato VS. Ultraconservative ablation in operative and esthetic dentistry. JOral Laser Applic 2003;3:73-78.

6. Lizarelli RFZ, Moriyama LT, Bagnato VS. Ablation of composite resins using Er:YAG laser - comparison with enamel and dentin. Lasers Surg Med 2003;33:132-139.

7. Lizarelli RFZ, Moriyama LT, Pelino, JEP, Bagnato VS. The use of laser-ablation rate to evaluate the quality of cure in light-polymerized composite resins. J Oral Laser Applic 2006;6:277-283.

8. Kildal KK, Ruyter IE. How different curing methods affect the degree of conversion of resin-based inlay/onlay materials. Acta Odontol Scand 1994;52:315-22.

9. Deb S, Sehmi H. A comparative study of the properties of dental resin composites polymerized with plasma and halogen light. Dent Mater 2003;19:517-522.

10. Uhl A, Michaelis C, Mills RW, Jandt KD. The influence of storage and indenter load on the Knoop hardness of dental composites polymerized with LED and halogen technologies. Dent Mater 2004;20:21-28.

11. Powell GL, Blankenau RJ. Argon laser polymerization of composite: blue lines vs. multilines. J Clin Laser Med Surg 1994;12:325-326.

12. Kelsey WP, Blankenau RJ, Powell GL, Barkmeier WW, Cavel WT, Whisenant BK. Enhancement of physical properties of resin restorative materials by laser polymerization. Lasers Surg Med 1989;9:623-627.

13. Powell GL, Anderson JR, Blankenau JR. Laser and curing light induced in vitro pulpal temperature changes. J Clin Laser Med Surg 1999;17:3-5.

14. Anic I, Bavelic B, Peric B, Matsumoto K. In vitro pulp chamber temperature rise associated with the argon laser polymerization of composite resin. Lasers Surg Med 1996;19:438-444.

15. Asmussen E, Peutzfeldt A. Influence of pulse-delay curing on softening of polymer structures. J Dent Res 2001;80:1570-1573.

16. Nomoto R. Effect of light wavelength on polymerization of light-cured resins. Dent Mater J 1997;16:60-73.

17. Cobb DS, Vargas MA, Rundle T. Physical properties of composites cured with conventional light or argon laser. Am J Dent 1996;9:199-202.

18. Vargas MA, Cobb DS, Schmit JL. Polymerization of composite resins: argon laser vs conventional light. Oper Dent 1998;23:87-93.

19. Fleming MG, Maillet WA. Photopolymerization of composite resin using the argon laser. J Can Dent Assoc 1999;65:447-450.

Contact address: PhD student Denis Pablo Jacomassi, Physics Institute of São Carlos, Optical Group, Biophotonic Laboratory, University of São Paulo, SP, Brazil. Trabalhador São Carlense, 400, Mailbox 369, 13560-970, São Carlos, SP, Brazil. Tel: +55-16-3373-9810, Fax: +55-16-3373-9811. e-mail: dejaco2001@yahoo.com.br