

Use of FT-Raman Spectroscopy to Determine the Degree of Polymerization of Dental Composite Resin Cured with a New Light Source

Safaa K.H. Khalil^a, PhD
Mousa A. Allam^a, PhD
Wael A. Tawfik^b, MD

ABSTRACT

Objectives: To use the FT-Raman spectroscopy for evaluation the degree of polymerization of dental composite as a result of photo curing with a new light source in comparison to the conventional halogen light.

Materials and Methods: In this study a new light source, based on a metal-halide lamp (TOPSPOT G12) was developed at NRC-Egypt for curing dental composites. Two groups of 108 composite samples each were cured using both the new light source and a conventional halogen source, as a control source. Different samples' sizes (2x2, 3x3 and 6x3 mm²) were cured for different periods of time (2, 4, 8, 12, 20, and 40 seconds). The spectroscopic data were analyzed statistically by ANOVA and Duncan's multiple range test (P< .05).

Results: The results showed that the samples cured by the new metal-halide source produced higher polymerization rates than those cured by the halogen source. The polymerization rate was directly proportional to the exposure time and inversely proportional to the sample size, irrespective to the light source used. The results also showed that 12 seconds of metal-halide light curing produced polymerization rate comparable to or even higher than that produced by 40 seconds halogen light curing.

Conclusions: The new light source produced a satisfactory degree of polymerization in a remarkable shorter curing time and it can be recommended for clinical use. (Eur J Dent 2007;2:72-79)

Key Words: FT-Raman spectroscopy; Degree of polymerization; Dental composite resin; Light-curing.

INTRODUCTION

Bonding of the orthodontic attachments by using light cure adhesive has gained more popularity in orthodontic practice today. It gives the opportunity for the operator to manipulate the bracket position to the right position and then start the po-

lymerization with a visible light source, usually at 450- 470 nm.¹ The most disadvantage of light cure system is time consuming where each bracket needs 40 seconds for curing. Many attempts were done in the last decade to decrease the curing time either by introducing new light sources or enhancements of the conventional halogen source. Oesterle et al² in a study of light-curing and setting times, recommended using a 40 second total light curing time (20 seconds on the mesial side and 20 seconds on the distal side of the brackets). Frost et al³ tried to reduce the curing time by using an elliptical light guide. They found that there was

- ^a Researcher, Department of Spectroscopy, Physics Division, National Research Centre, Egypt.
- ^b Assistant Professor, Department of Oral and Dental Research, National Research Centre, Egypt.
- Corresponding Author: Dr. Safaa K.H. Khalil, Department of Spectroscopy, Physics Division, National Research Centre, 12311, Dokki, Giza, Egypt. Tel: +2 010 540 64 79 E-mail: safaakhk@yahoo.com

significant reduction in total bonding time. Another trial was done by Bishara et al.⁴ They tested the standard cured light guide with an 11 mm diameter and 4 mm mini turbo light guide and found no significant differences in shear bond strength between them. Evans et al⁵ investigated the shear bond strengths of orthodontic brackets by using different light guides (Power slot and turbo tip) and found that the light guides could significantly reduce the curing times without affecting the shear bond strength.

Many authors thought to introduce another light source like Laser or plasma arc light and finally the micro-xenon light. Blankenau et al⁶ compared the degree of polymerization by argon laser and conventional light-curing unit and found that the polymerization with argon laser produced an even greater polymerization than halogen light. In contradict to the concept which states that Laser may produce more heat generation, Powell et al⁷ stated that, at recommended curing times; in vitro pulp-chamber temperature increases from argon lasers were significantly lower than those of the conventional curing lights.

Featheringham⁸ compared 3 different visible light curing systems; the argon laser at 4, 6, 8 and 10 seconds, plasma arc curing unit at 2, 4, 6 or 8 seconds and conventional halogen light at 40 seconds. He concluded that the curing by plasma arc at 4 seconds resulted in significantly higher mean shear bond strength than curing with the plasma arc at 2 seconds or the argon laser at 4 seconds, argon at 8 seconds showed higher bond strengths than it did at 4 seconds. Cacciafesta et al⁹ investigated the polymerization with micro-xenon light of a resin-modified glass ionomer. They found no statistically significant differences between the bond strength of control group cured with halogen light and those of groups cured with xenon light for 10, 5 and 2 seconds respectively. They concluded that the micro-xenon light enabled the clinician to reduce the curing time without affecting the shear bond strength. Recently, Staudt et al¹⁰ tested the shear bond strength with a high-power halogen light curing source. They concluded that the high power halogen light seemed to be cost-effective solution to reduce curing time to 2-3 seconds.

Laser source, plasma arc light and micro-xenon light are very expensive and need special equipments that may not be available in dental

office. Therefore, introducing a new light source capable of reducing the curing time with reasonable economic cost is a premium goal for the dental field.

It is important to evaluate the degree of polymerization of polymeric adhesives, since inadequate polymerization results in inferior physico-mechanical properties.^{11,12} Orefice et al¹³ monitored the monomer conversion of dental composites during visible light irradiation in situ by infrared spectroscopy and evaluated the microhardness of the composites with different degrees of conversion. They obtained a direct relationship between microhardness and degree of monomer conversion. FT- Raman spectroscopy is also one of the methods that can be utilized to obtain structural information for opaque materials such as enamel, dentin and related polymeric composites.¹⁴

The main objective of this study was to use FT-Raman spectroscopy technique to measure the degree of polymerization of a dental composite resin cured with a new light-curing source designed at the National Research Center of Egypt.

MATERIALS AND METHODS

Metal-Halide light curing source

In this study, a new metal-halide light curing source was adopted for photo polymerization of the dental adhesive used. This light source is composed mainly of a metal-halide lamp for special applications (BLV, Steinhoring, Germany). The energy consumption of this lamp is 150W and current 1.8A, with power density 1500 mW /cm². The advantages of metal-halide lamp are very high color temperature, high color stability over the entire life time, long life time (average life time 6000 hours) and special light spectrum as shown in Figure 1.

A conventional halogen light source for dental cure, power density 0.6 W/cm² (Caulk Dentsply, Milford, DE, Canada) was used as a reference light curing unit for comparison with the newly introduced metal-halide source.

Sample preparation

Alpha-Dent (Dental Technologist Inc., Lincoln, IL, USA) is a composite resin-based adhesive commercially available. It is used in this study to evaluate the efficiency of the new metal-halide lamp for polymerization of the composite. Three

sizes cylindrical specimens of the composite were prepared (2x2, 3x3 and 6x3 mm², diameterx height) using closed-end Teflon moulds. The open end was filled with the uncured composite to an excess with slight pressure (to avoid air bubbles). The excess amount was removed with a clean dry glass slide. Then, the specimen was light cured by a direct contact with the light source under investigation for the following periods of time: 2, 4, 8, 12, 20 and 40 seconds. The complete hard set specimen was released from the mould, ground into fine powder and packed in NMR glass tube (5 mm² internal diameter) ready for FT-Raman spectroscopy measurements. Each specimen of a certain irradiation time was prepared three times to obtain three Raman spectra. Processing the samples and recording their spectra occurred within 24 hours from the beginning of the light curing at room temperature (21±1C°). Uncured composite specimen was filled directly into the NMR glass tube and underwent Raman analysis. This experiment was repeated six times.

FT-Raman measurements

All the FT-Raman measurements were carried out by using the Nexus 670 FTIR FT-Raman spectrometer (Nicolet, USA). The excitation source in the FT-Raman module is Nd-YAG laser. This emits continuous-wave laser energy at wave length of 1064 nm (9398 cm⁻¹) and has a maximum power level of approximately 1.5W at the sample. The installed detector in the FT-Raman module is In-GaAs, which is an air-cooled detector. The beam splitter is XT-KBr. The used sample configuration is 180° reflective with fully motorized sample posi-

tion adjustment, with an NMR-tube sample holder. All the FT-Raman spectra were collected in the spectral range from 3701 to 98 cm⁻¹ and 46 scans. The laser power was 0.7 W. The spectra were processed using the computer program Omnic ESP, 5.2a (Nicolet, USA).

Calculation of the degree of polymerization (DP)

The DP of the composite can be determined by comparison of the ratio (R) of the reacting aliphatic C=C bonds to the unreacting aromatic C=C bonds before and after curing. The aliphatic and aromatic C=C bonds have characteristic Raman scattering peaks located at 1638 and 1610 cm⁻¹, respectively as well as the infrared absorption peaks but with higher intensities. The peak height (H) and underlying area (A) was calculated for each peak, using a standard baseline technique with aid of computer program provided with the spectrometer. The ratio (R) was determined twice by means of the peaks heights and areas for confidential results.

The percentage DP of each specimen was calculated using the following equation.¹⁵⁻¹⁷

$$DP\% = (1 - (R_{\text{polymer}} / R_{\text{monomer}})) \times 100$$

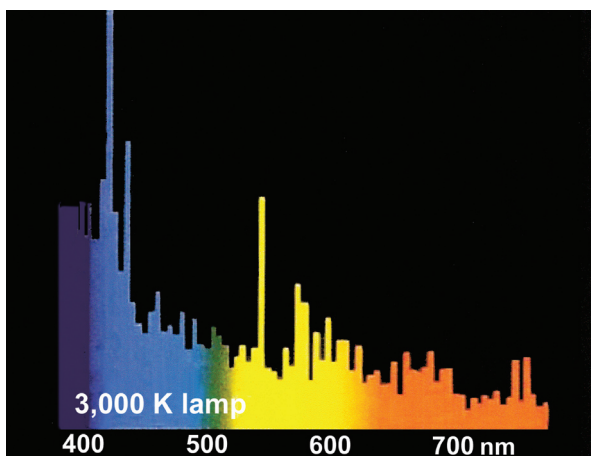
Statistical analysis

The obtained data were subjected to analysis of variance (ANOVA) according to Snedcor and Cochran.¹⁸ Duncan's multiple range test was used to compare between means of treatments according to Walter and Duncan¹⁹ at probability 5%.

RESULTS

The typical FT-Raman spectra recorded for the composite before and after photoinitiation by the metal-halide light source are shown in Figure 2. The spectra reveals a scattering Raman peak at 1638 cm⁻¹ corresponding to the reacting aliphatic C=C stretching of the vinyl group in the acrylates and methacrylates.^{12,20} The spectra show a remarkable decrease in the intensity of this peak as a result of the exposure to the new light source. The scattering peak at 1610 cm⁻¹ referring to the unreacting aromatic rings in the BIS-GMA molecule is commonly used as an internal reference for precise quantitative analysis.^{15,17,21}

For more confidential data, the ratio of the peaks 1638 to 1610 cm⁻¹ (R) was calculated twice,



Wave Length (nm)
Figure 1. Spectral distribution of the metal-halide lamp.

by means of peaks height and peaks area. Tables 1 and 2 give the mean values of the percentage degree of polymerization (DP%) of the resin cured by each light source calculated by the peaks height and peaks area, respectively. These values are plotted against the time of exposure in Figures 3 and 4, respectively. Both figures exhibit the same behavioral pattern of DP% with curing time either the composite was halogen-cured or metal-halide cured. There is a rapid increase in the DP% with increasing the curing time up to 12 seconds, followed by gradual increase up to 40 seconds for

any sample size. It could be noticed that the smallest sample size (2x2 mm²) had always the highest values of DP%.

The results of statistical analysis of the data given in Tables 1 and 2 revealed that the samples cured by the metal-halide source produced higher polymerization rate values than those cured by the halogen source. The polymerization rate was directly proportional to the exposure time and inversely proportional to the sample size irrespective to the light source used. It could be noticed that the polymerization rate values of the samples

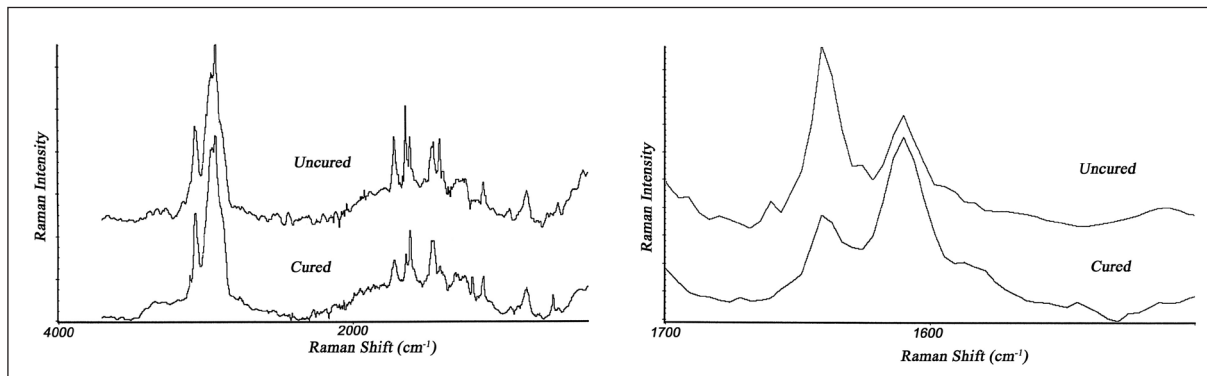


Figure 2a. Typical FT-Raman Spectrum of uncured composite sample and 40 seconds cured sample by metal-halide source.

Figure 2b. Magnified section from the FT-Raman Spectrum of uncured composite sample and 40 seconds- cured sample by metal-halide source.

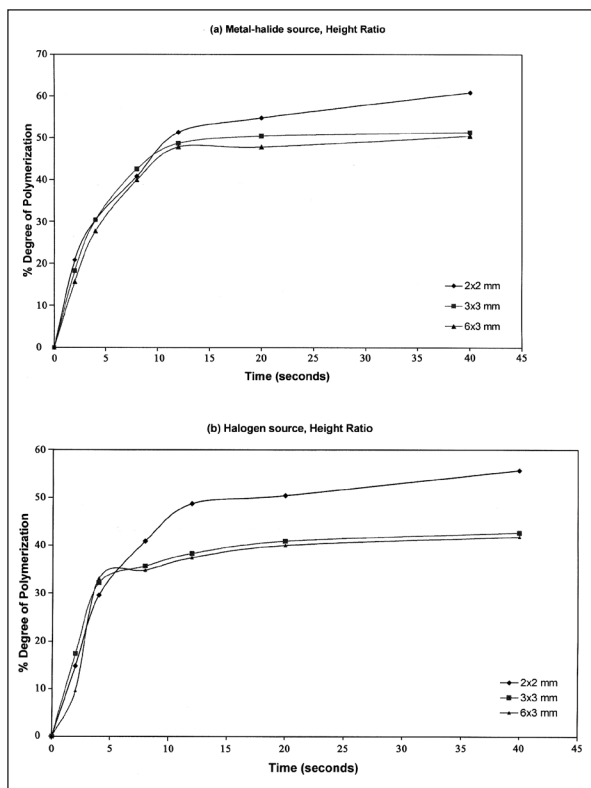


Figure 3. Variations of DP% (via peaks height ratio) of the composite with the curing time as a result of exposure to the metal-halide and halogen light sources.

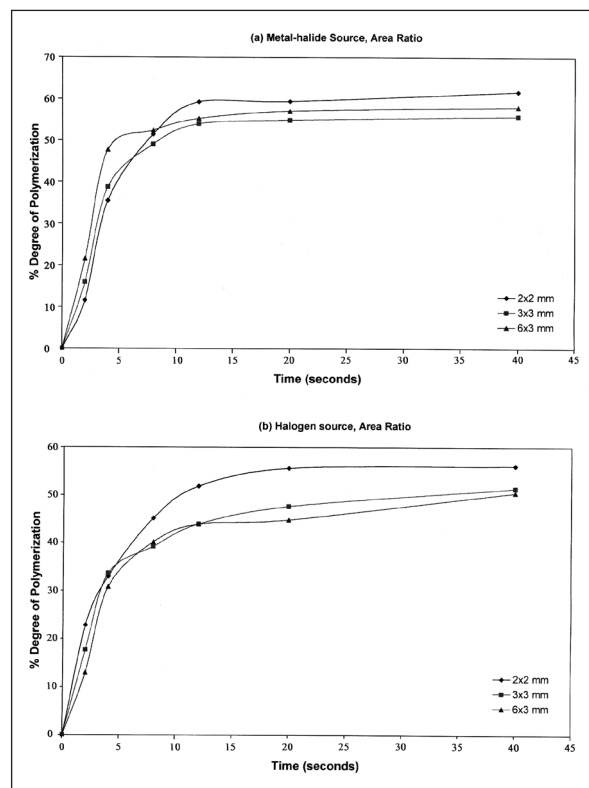


Figure 4. Variations of DP% (via peaks area ratio) of the composite with the curing time as a result of exposure to the metal-halide and halogen light sources.

given in Table 2 were higher than their corresponding values given in Table 1. This observation can be explained by the fact that the area of the peak is supposed to be more representative to the actual scattering of the peak than its height. Therefore, we can rely on the results reported in Table 2 conveniently. From this table, the newly in-

troduced metal-halide source produced satisfactory polymerization (51.40%) of the composite in a rather short curing time, 8 seconds. There was no significant difference in the polymerization values between the samples cured by the metal-halide source for 12, 20 and 40 seconds (59.19, 59.35 and 61.68%, respectively). Results in both Tables 1 and

Table 1. The mean values of DP% (via peaks height ratio) of different sized composite samples photopolymerized either by metal-halide (M) or halogen (H) light sources at various periods of curing time.

Time (seconds)	2x2 (mm ²)		3x3 (mm ²)		6x3 (mm ²)	
	M	H	M	H	M	H
	DP% Test SD	DP% Test SD	DP% Test SD	DP% Test SD	DP% Test SD	DP% Test SD
2	20.87 m (5.22)	14.78 o (0.87)	18.26 mn (3.48)	17.39 no (0.87)	15.65 no (1.74)	9.57 p (3.48)
4	30.43 jkl (1.74)	29.57 kl (1.74)	30.43 jkl (0.87)	32.17 ijk (1.74)	28.12 l (1.33)	33.04 hij (1.74)
8	40.87 e (1.76)	40.87 e (0.87)	42.61 e (0.78)	35.65 gh (0.87)	40.00 ef (0.89)	34.78 ghi (0.87)
12	51.30 c (0.87)	48.70 cd (1.74)	48.70 cd (1.74)	38.26 ef (3.62)	47.83 d (1.74)	37.39 fg (0.89)
20	54.78 b (1.74)	50.44 cd (1.64)	50.43 cd (0.87)	40.87 e (0.87)	47.83 d (0.85)	40.00 ef (1.74)
40	60.87 a (0.87)	55.65 b (1.73)	51.30 c (0.88)	42.61 e (1.74)	50.43 cd (0.87)	41.74 e (0.87)

SD is the standard deviation

When two values have different letters, this means that they are statistically different numbers. If they have a common letter, this means that there is no significant difference between their numbers.

Table 2. The mean values of DP% (via peaks area ratio) of different sized composite samples photopolymerized either by metal-halide (M) or halogen (H) light sources at various periods of curing time.

Time (seconds)	2x2 (mm ²)		3x3 (mm ²)		6x3 (mm ²)	
	M	H	M	H	M	H
	DP% Test SD	DP% Test SD	DP% Test SD	DP% Test SD	DP% Test SD	DP% Test SD
2	11.53 r (1.50)	22.90 o (0.47)	15.89 pq (1.50)	17.76 p (1.78)	21.50 o (0.93)	13.08 qr (1.50)
4	35.51 m (0.93)	33.02 mn (1.50)	38.78 l (0.47)	33.64 mn (0.93)	47.66 gh (1.87)	30.84 n (0.93)
8	51.40 f (0.91)	45.17 hij (1.56)	49.00 gh (0.94)	39.25 kl (1.87)	52.34 ef (0.93)	40.19 kl (1.87)
12	59.19 abc (1.50)	51.87 f (0.47)	53.92 ef (1.87)	43.93 ij (0.93)	55.14 de (1.87)	43.93 ij (3.75)
20	59.35 ab (0.47)	55.61 d (1.40)	54.79 de (1.50)	47.66 gh (3.74)	57.01 bcd (1.89)	44.86 hij (1.88)
40	61.68 a (0.93)	56.07 cd (3.74)	55.71 d (1.50)	51.40 f (3.74)	57.94 bcd (0.94)	50.47 fg (1.78)

SD: is the standard deviation

When two values have different letters, this means that they are statistically different numbers. If they have a common letter, this means that there is no significant difference between their numbers.

2 revealed that for all sample sizes, curing with metal-halide light for 12 seconds achieved polymerization rates comparable to or even higher than that produced by 40 seconds halogen curing. This finding is practically important since the thickness of the adhesive under the bracket is too thin, so 12 seconds of metal-halide curing is helpful to obtain enough polymerization for bonding brackets in short time.

The overall DP value data of the resin produced by exposure to each light source irrespective to the exposure time (from 2 to 40 seconds) or sample size are given in Table 3. The statistical evaluation of the data using an independent sample (Duncan test) demonstrated that the metal-halide source produced a significant increase in the overall polymerization in comparison with that produced by conventional halogen light source.

DISCUSSION

Vibrational spectroscopy, such as FT-infrared and FT-Raman, provides key information on the structure of molecules. The position and intensity of the feature in the vibrational spectrum can be used to study the molecular structure or to determine the chemical identity of the sample. The two techniques are, in fact, complementary to each other. Vibrations that are strong in an infrared spectrum (involving strong dipole moments) are usually weak in a Raman spectrum. Likewise, non-polar functional group vibrations that give very strong Raman bands usually result in weak infrared signals. For example, OH- or NH-stretching vibrations and the vibration of carbonyl groups are usually very strong in an FT-IR spectrum and are usually weak in Raman spectrum. However, the stretching vibrations of C=C such as in dental composites are very strong in the Raman spectrum.^{22,23}

The results of this investigation revealed that

there were statistically significant differences between the degree of conversion values of metal-halide source and halogen source. The lamp of metal-halide source is completely different from the halogen lamp at many aspects; the power density of the metal-halide is 1500 mW/cm² while for halogen light is only 600mW/cm². The halogen lamp has a limited effective lifetime approximately 100 hours due to degradation of the bulb's components by high heat generated.^{12,24-26}

The metal-halide lamp has several advantages such as space saving design, economic due to long lifetime (average lifetime 6000 hours), high color stability over the entire life time, axial arc, and ability to produce good light beam and UV protection.

According to Fujibayashi et al²⁷ who stated that the quality of light polymerization was not exclusively due to light intensity but also due to the narrow absorption peak of the initiator system (camphorquinone). The absorption curve of camphorquinone extends between 360 and 520 nm, with the maximum at 465 nm.^{12,28} For metal-halide source, most photons emitted were within the maximum absorption curve of camphorquinone; while the photons emitted by conventional halogen light were around the optimal spectrum range.

According to the results of many investigations comparing new light sources reached to an accepted degree of conversion in reduced time as, fast halogen light 10-15 seconds, plasma arc light 6-9 seconds and LED light 20 seconds with the conventional halogen light 40 seconds.^{12,29,30} They concluded that LED was the most suitable as a good alternative to the halogen light, where the plasma arc light were bulky and usually incorporated a noisy cooling fan, both plasma arc light and fast halogen light were more expensive than the conventional halogen light. They preferred the LED because it was smaller, cordless and did not

Table 3. The overall degree of polymerization of the resin produced by metal-halide and conventional halogen light sources.

Light source	Peaks Area calculations			Peaks height calculations		
	DP%	SD	Test	DP%	SD	Test
Metal-halide	44.91	14.91	a	40.60	13.30	a
Halogen	40.09	12.51	b	35.59	11.88	b

SD: standard deviation.

Different letters means statistically significant different values and a > b.

require cooling fan and had an estimated life over 10000 hours.³¹

In comparison with the previously mentioned sources, the metal-halide source is not expensive like the plasma arc light or fast halogen light, and it has long life period 6000 hours near LED. Moreover, it has the ability to produce higher degree of conversion in markedly reduced curing time (12 seconds). Therefore, the new metal-halide source can be recommended for orthodontic field since bonding of 20 brackets needs 800 seconds with conventional halogen light while with new source requires only 240 seconds.

CONCLUSIONS

The new metal-halide light source produces comparable degree of polymerization in a significant shorter curing time and therefore can be recommended for clinical use.

REFERENCES

1. Pollack BF, Blitzer MH. The advantages of visible light curing resin. *N Y State Dent J* 1982;48:228-230.
2. Oesterle LJ, Messersmith ML, Devine SM, Ness CF. Light and setting times of visible light-cured orthodontic adhesives. *J Clin Orthod* 1995;29:31-36.
3. Frost T, Norevall LI, Persson M. Bond strength and clinical efficiency for two light guide sizes in orthodontic bracket bonding. *Br J Orthod* 1997;24:35-40.
4. Bishara SE, Vonwald L, Zamtua J. Effects of different types of light guides on shear bond strength. *Am J Orthod Dentofacial Orthop* 1998;114:447-451.
5. Evans LG, Peter C, Flickinger C, Taloumis L, Dann W. A comparison of shear bond strengths of orthodontic bracket using various light sources, light guides, and cure times. *Am J Orthod Dentofacial Orthop* 2002;121:510-515.
6. Blankenau R J, Kelsey W P, Powell G L, Sheare G O, Barkmeier W W, Cavel WT. Degree of composite resin polymerization with visible light and argon laser. *Am J Orthod Dentofacial Orthop* 1991;4:40-42.
7. Powell GL, Anderson JR, Blankenau RJ. Laser and curing light induced in vitro pulpal temperature changes. *J Clin Laser Med Surg* 1999;17:3-5.
8. Featheringham DA. Comparison of three curing light systems for polymerization of orthodontic adhesives: an in vitro study thesis abstract. *Am J Orthod Dentofacial Orthop* 2001;120:331.
9. Cacciafesta V, Sfondrini MF, Klersy C, Sfondrini G. Polymerization with a micro-xenon light of a resin modified glass ionomer: a shear bond strength study 15 minutes after

bonding. *Eur J Orthod* 2002;24:689-697.

10. Staudt BC, Mavropoulos A, Kiliaridis S. Shear bond strength with a high-power Halogen light curing sources. Oral presentation 80th European Orthodontic Society Congress: Aarhus- Denmark 2004.
11. Soh MS, Adrian U, Yap J. Influence of curing modes on crosslink density in polymer structures. *J Dent* 2004;32:321-326.
12. Üsümez S, Büyükyılmaz T, Karaman AI, Gündüz B. Degree of conversion of two lingual retainer adhesives cured with different light sources. *Eur J Orthod* 2005;27: 173-179.
13. Orefice RL, Discacciati JAC, Neves AD, Mansur HS, Jansen WC. In situ evaluation of the polymerization kinetics and corresponding evolution of the mechanical properties of dental composites. *Polymer Testing* 2003;22:77-81.
14. Xu J, Stangel I, Butler IS, Gilson DFR. An FT-Raman spectroscopic investigation of dentin and collagen surfaces modification by 2- Hydroxyethylmethacrylate. *J Dent Res* 1997;76:596-601.
15. Ferracane JL, Greener EH. Fourier transform infrared analysis of degree of polymerization in unfilled resins-methods comparison. *J Dent Res* 1984;63:1093-1095.
16. Meniga A, Tarle Z, Ristic M, Sutalo J, Pichler G. Pulsed blue laser curing of hybrid composite resins. *Biomaterials* 1997;18:1349-1354.
17. Yoon TH, Lee YK, Lim BS, Kim CW. Degree of polymerization of resin composites by different light sources. *J Oral Rehabil* 2002;29:1165-1173.
18. Snedcor GW, Cochran WG. Statistical methods, 9th ed. Iowa State: University press, Iowa, USA, 1990.
19. Walter A, Duncan DB. Multiple range and multiple test. *Biomaterials* 1969;11: 1-24.
20. Decker C. Kinetic analysis and performance of UV-curable coatings. 1992. In: Pappas S.P (ed.) Radiation curing, science and technology. Plenum Press. New York, pp. 135-179.
21. De Santis A, Baldi M. Photopolymerization of composite resins measured by micro-Raman spectroscopy. *Polymer* 2004;45:3797-3804.
22. Ferraro JR, Nakamoto K. Introductory Raman Spectroscopy: Academic Press, Inc, 1994.
23. Wartewig S. IR and Raman Spectroscopy Fundamental Processing. 2003, Wiley-VCH GmbH & Co. KGaA, Weinheim.
24. Mills RW, Jandt KD, Ashworth SH. Dental composite depth of cure with halogen and blue light emitting diode technology. *Br Dent J* 1999;186:388-391.
25. Jandt KD, Mills RW, Blackwell GB, Ashworth SH. Depth of cure and compressive strength of dental composites cured with blue light emitting diodes (LEDs). *Dent Mater*

- 2000;16:41-47.
26. Stahl F, Ashworth SH, Jandt KD, Mills RW. Light emitting diode (LED) polymerization of dental composites: flexural properties and polymerization potential. *Biomaterial* 2000;21:1379-1385.
 27. Fujibayashi K, Ishimaru K, Takahashi N, Kohono A. A newly developed curing unit using blue light emitting diodes. *Dentistry in Japan* 1998;34:49-53.
 28. Nomoto R. Effect of light wavelength on polymerization of light-cured resins. *Dent Mater* 1997;16:60-73.
 29. Wendel B, Dorschel H, Kern W. A comparative study of polymerization lamps to determine the degree of cure of composites using infrared-spectroscopy. *Eur J Orthod* 2004;26:545-551.
 30. Pettemrides AP, Sherriff M, Ireland AJ. An in vivo study to compare a plasma arc light and a conventional quartz halogen curing light in orthodontic bonding. *Eur J Orthod* 2004;26:573-577.
 31. Haitz RH, Craford MG, Wiessman RH. Handbook of optics. McGraw Hill: New York 1995: vol. 2.