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Degree of conversion of resin composites light activated by halogen light and led analyzed by ultraviolet spectrometry

Grau de conversão de resinas compostas fotoativadas por luz halógena e LED analisadas por espectrometria ultravioleta

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Abstract

Objectives: The aim of this study was to compare the degree of conversion of different shades of a composite resin activated with two different light sources. **Material and method**: Composite resin (Charisma™), A2 and SL were photoactivated with a halogen lamp and a LED based system, at three different light activation times (10, 20 and 40s). The degree of conversion was analyzed by ultraviolet spectroscopy with variation in wavelength. The data were submitted to ANOVA and the Games Howell test (5%). **Results**: The resin composite shade SL presented a higher degree of conversion in depth than the resin composite shade A2. The three light activation times had no influence on the degree of conversion in the groups of resin composite SL light activated with halogen light and LED. **Conclusion**: It was concluded that the resin composite SL presented the highest degree of conversion, irrespective of the light polymerization time and the light source used.

Keywords: Degree of conversion. Composite resin. Light polymerization.

Resumo

***Objetivos**: O objetivo deste estudo foi comparar o grau de conversão de uma resina composta com diferentes cores, utilizando duas fontes ativadoras. **Material e método**: Utilizou-se uma resina composta (Charisma®) nas cores A2 e SL, fotoativada com lâmpada halógena e com sistema LED, em três tempos de fotoativação (10, 20 e 40s). O grau de conversão foi analisado por meio da espectrometria ultravioleta, com variação no comprimento de onda. Os dados obtidos foram submetidos à ferramenta ANOVA e ao teste Games Howel (5%). **Resultados**: A resina composta cor SL apresentou maior grau de conversão que a resina composta cor A2. Os três tempos de fotoativação não influenciaram no grau de conversão nos grupos de resina composta SL fotoativadas com luz halógena e LED. **Conclusão**: A resina composta SL apresentou maior grau de conversão independente do tempo de fotopolimerização e da fonte de luz utilizada.*

***Palavras-chave**: Grau de conversão. Resina composta. Fotopolimerização.*

Introduction

One of the most critical aspects of a composite resin restoration is the polymerization stage. Incomplete polymerization may result in a resin with high porosity, less hardness, low polishing and high staining capacity and even toxic effects on pulp caused by the free monomers (1-4).

Adequate light activation transforms the monomers into a complex polymer structure. Monomer conversion into polymers does not attain 100%, but results in monomers that remain unreacted (1). Resin composites start the polymerization process by absorbing light in a specific range of wavelength around 400 to 500 nm; once activated, react with the reducer agent (aliphatic amine) to produce free radicals.

The number of double carbon links (C=C) present in the monomers, which are converted into single links (C-C) to form the polymeric chain during the polymerization process, is called *degree of conversion* (3, 5). The extent to which monomers react to form the polymer during the polymerization reaction has an important effect on the physical and mechanical properties of composites resins (6-9).

Among the methods to evaluate the degree of conversion of composite resins found in the literature are optic and electronic microscopy, differential thermogravimetric analysis (DTA), high performance liquid chromatography (HPLC) and the vibratory methods, such as Fourier transformation infrared spectrometry (FTIR), Raman spectroscopy and ultraviolet-visible spectrometry (UV-Vis).

Ultraviolet-visible spectrometry presents the important characteristic of making it easy to determine double links quantitatively, as in the case of monomers that constitute the composite resines. The quantity of residual monomers determined by spectrometry equipment appears to be the most sensible method for analyzing the degree of conversion of resin composites at present (10, 11).

The aim of this study was to compare the degree of conversion of two shades of a composite resin, light activated by two sources of light at different exposure times, using quantitative analysis by ultraviolet-visible spectrometry.

Material and method

Two-mm thick specimens were obtained using a two-piece teflon matrix, 6 mm in diameter and 6 mm deep. The active tip of the light polymerizer was placed on the external surface of the matrix at a distance of 4 mm from the specimens, simulating a Class II restoration. The two light sources used for polymerization were: Optilux 401™ (Demetron Research Corporation, Danbury, CT, USA) halogen lamp and a LED based light polymerizer appliance (Optilight LD III™) (Gnatus, Ribeirão Preto, São Paulo, Brazil). The specifications of these sources are shown in Table 1.

The specimens were prepared with a microhybrid composite resin (Charisma™) (Heraeus Kulzer, Hanau, Germany), shades A2 (lot: 010202) and SL (lot: 010040); polymerized in the teflon matrix for 10, 20 and 40s with ten repetitions for each experimental group, totaling 120 specimens, which were weighed on an analytical scale and immediately put into 10 mL of methanol (PA, dry and distilled) for 24 hours, protected from light with aluminum sheet and kept at ambient temperature. After the residual monomer solution was placed in a volumetric flask and diluted in methanol to make up 50 mL, in order to reduce the concentration and facilitate reading in the spectrometer. An ultraviolet-visible spectrometer was used to read the samples and the results were analyzed with the Origin 5.0™ program.

To obtain the calibration curve, 1 g of the resin composite Charisma™ was dissolved in 10 mL of chloroform in a test tube protected from light. To separate the inorganic loads and organic compounds from the resin composite, it was centrifugated at 6500 rpm for 15 min. For the shades A2 and SL the quantity of pure monomer found was 270 mg and 315 mg respectively.

The supernatant solution containing the monomers was taken to a rotary evaporator at the ambient temperature until dried. After the chloroform had evaporated, 10 mL of methanol was placed in the flask to dissolve the residual monomer, that is, the Bis-GMA and TEGDMA contained in the resin. The solution was transferred to a 100 mL volumetric flask and the volume made up with methanol. The initial solution went through several dilutions to obtain the following concentrations: 0.20; 0.30; 0.40; 0.50; 0.60 mg/L.

Table 1 - Specifications of the halogen and LED based light sources

Appliance	Light source	Active tip	Light intensity (mW/cm²)	Wavelength (nm) (According to Manufacturer)
Optilux 401™ (Demetron)	Halogen	6 mm	500	400-500
Optilight LD III™ (Gnatus)	LED	6 mm	650	470-490

Optilux 401™, Demetron Research Corporation, Danbury, CT, USA.
Optilight LD III™, Gnatus, Ribeirão Preto, São Paulo, Brazil.

At each dilution of the monomer, a reading was taken in an ultraviolet spectrometer at a wavelength between 200 and 600 nm (UV-Vis -2401 PC™) and coupled to a microcomputer in the (UVPC Personal Spectroscopy Software Version 3.9 ™) program. The data obtained were analized by the Origin 5.0™ program to establish the calibration curve and analyze the extracts of the light activated specimens. The absorbance values (% A) found were obtained by the lowest dilutions of the pure monometer detected by the ultraviolet equipment. After ultraviolet reading of the peaks of greatest intensity at the different dilutions of the monomer, the data were transferred to the Origin 5.0™ program by means of a mathematical equation. The straight lines obtained in the absorbance graphs vs. the concentration allowed the residual monomers to be quantified as follows:

Y = absorbance of the solution extracted from the test specimens
A = linear coefficient of the straight line
B = angular coefficient of the straight line
x = concentration of the sample analyzed
C = degree of conversion

$$x = \frac{Y - A}{B}$$

$$C = \frac{\text{absorbance} - \text{absorbance } (x = 0)}{\text{concentration } (y = 0)}$$

The results were analyzed by the analysis of variance (ANOVA) for three criteria, and by the Games Howell multiple comparisons statistical tests, at a level of significance of 5%.

Results

The Charisma™ in shades A2 and SL presented heterogeneous distribution, with a higher percentage of residual monomers in shade SL when compared with shade A2. The mean values were expressed in the form of degree of conversion of the polymers (% in mass) and are shown in Table 2. The groups of resin composite A2 light activated with halogen light and LED, at different times of 10, 20 and 40s did not differ statistically among them ($p > 0.05$) and showed the lowest degree of conversion values.

The groups SL light activated with halogen light and LED did not differ statistically among them ($p > 0.05$) and showed the highest degree of conversion values. The groups A2 light activated with halogen light and LED and the groups SL light activated with halogen light and LED did not differ statistically among them ($p > 0.05$) and showed the highest degree of conversion values.

Table 2 - Means, standard deviations, coefficient of percentage variation of the percentage of residual monomer according to resins, appliances and times

Resin	Source	Time	Mean		Standard Deviation	C.V.(%)
A2	Halogen	10 s	78,39	A,B,C	2.56	3.27
		20 s	81,15	A,B,C,D,E	6.22	7.66
		40 s	81,29	A,B,C,E	5.51	6.78
	LED	10 s	75,95	A,B,C	3.51	4.63
		20 s	77,43	A,B,C	3.54	4.57
		40 s	78,79	A,B,C	3.82	4.85
SL	Halogen	10 s	89,12	B,D,E,F	2.34	2.62
		20 s	88,64	B,C,D,E,F	5.40	6.09
		40 s	90,37	D,E,F	3.27	3.62
	LED	10 s	87,01	B,C,D,E,F	0.92	1.06
		20 s	88,25	B,C,D,E,F	1.40	1.59
		40 s	87,59	B,C,D,E,F	1.68	1.92

Different letters indicate statistically significant difference ($p<0.05$).

Discussion

The quantity of monomers still present in resin composite samples submitted to various light polymerization conditions was determined. The degree of conversion of monomers into polymers, expressed in percentage mass, was evaluated. This was done by studying two shades of a resin composite, activated with a halogen lamp and a LED based system, at three light activation times. The analytical technique chosen to identify and quantify these monomers was ultraviolet-visible spectrometry.

To establish a correlation between the mechanical properties of the resin composites and the polymerization quality (12-20), it is important to analyze the degree of conversion through the chemical components of the materials. The links formed between the molecules of the material take place in the initial stage of light activation, and continue to propagate, forming the polymer. The light intensity of the equipment is directly related to the quality of this polymer formation (7, 20).

Different methodologies have been used to study the degree of conversion of resin composites. In the majority of studies (7, 11, 21) the test specimens are manually ground together with potassium bromide (a material inert to infrared light). Due to the hardness of polymerized resin, it was experimentally observed that it would be easy to lose fractions of the sample during the grinding process. When part of the mixture remains in the receptacle, the reliability of the quantitative spectrum of the analysis is certainly affected, thus making it difficult to compare the values through the spectra performed.

In this research the ultraviolet-visible (UV-Vis) spectrometry technique was used, which has the advantage of calculating the carbon deficiency index from the molecular formula and determining the presence or absence of certain unsaturated groups. In ultraviolet spectrometry, conjugated structures are rapidly established, for example, the C=C or aromatic structures. Confirmation is obtained by comparison with the spectrum of an identical sample (22) with the advantage that one obtains these readings more easily by ultraviolet spectrometry.

The resin composite calibration curve was constructed by fractioning the resin in two shades. The pure monomer, the organic compound without having been light polymerized, was determined by means of the total quantity for each shade of the resin composite. In the dilutions of the resin composite Charisma™ shade SL, the absorbance values were higher, probably because it contained a larger quantity (315 mg) of organic load in its composition.

The resin composite Charisma™ shade SL presented greater mass conversion when compared with shade A2. This was probably because contains a larger quantity of organic compound (315 mg), compared with the resin composite Charisma™ shade A2 (270 mg), which influenced the chemistry of the materials, and therefore presented greater conversion. It is known that polymerization characteristics are influenced by chemistry (14) and by the material concentration (23). This demonstrates that resin composites that have Bis-GMA and TEGDMA as organic matrixes in their composition can contain different quantities of monomers. Probably the quantity of TEGDMA and the type of inorganic particles are the main factors of conversion of resin composites (24, 25). TEGDMA was considered the main contributor to polymerization after irradiation in Bis-GMA/TEGDMA based resin composites (26, 27). This could indicate a larger quantity of TEGDMA in the resin composite Charisma™ shade SL, as was demonstrated in this study.

The residual monomers that do not form the polymeric chain, and are therefore free in the chain, were present in a larger quantity in the resin composite Charisma™ shade A2. In the present study, the resin composite Charisma™ shade SL promoted a higher degree of conversion, around 89.49%, well above that of the resin composite shade A2 (78.83%).

The results demonstrated that irrespective of resin composite shade, the percentage of residual monomers at the three light activation times (10, 20 and 40s) remained at similar percentages. Studies conducted by Nomoto et al. (8) and Calheiros et al. (28) demonstrated that after 5s of incident light, camphorquinone activation was initiated and that an increase in light activation time did not enhance the degree of conversion, but only increased polymerization shrinkage. The increase in time of exposure to light does not increase the degree of conversion and in fact obtains a saturation reaction of resin composite polymeric chains.

As several studies in the literature have shown, the exposure time is important for improving the mechanical properties of resin composites, but light intensity is a relevant factor for effective polymerization and the best results achieved were with 20 and 30 seconds and irradiation of 500 and 600 mW/cm² (29).

It is important to achieve adequate polymerization of the resin composite to ensure successful restorations and their longevity. Otherwise, inadequate polymerization may result in inferior physical properties (13, 14, 16, 30-32). The combination of small particles of inorganic load with different geometries (micro-hybrids) was important for increasing wear-resistance without compromising the percentages of double carbon links (18). This comparison leads to the reasoning that the physical properties of the materials are directly related to a higher degree of conversion, but the free monomers in the polymeric chain could also present loss of structure and diminish the longevity of the material (5, 23). In micro-hybrid resin composites, it has been shown that when the time of exposure to light is increased from 10s to 40s, the conversion values remain constant and independent of the light source used.

It was observed that there was statistical difference between the experimental groups light activated with the LED system and halogen lamp. For the two resin shades, the use of the halogen lamp promoted a mass conversion in the range of 2 to 3% higher than the LED based system. In accordance with the statistical analysis, it is possible to affirm that in the studies conducted, the halogen lamp was shown to be more efficient than the LED based system.

Halogen light appliances represent important items of polymerization equipment in dentistry at present. It is known that the large majority of halogen light equipment items used in dentists' offices require more maintenance. One of the problems presented by this type of light source is the heat dissipated by the lamp, because the filament requires heating. The high temperatures reached may also cause rapid degradation of the filament and consequently a shorter working life.

It is known that LED based light activation appliances appeared on the dentistry market with the purpose of replacing the conventional appliances and the prospect of quality polymerization. Rueggeberg et al. (33) recommended that appliances with a light intensity below 233 mW/cm² and a light activation time of less than 60s must not be used in clinical routine. The carbon links that are not activated by the light activator light and remain free in the polymeric chain represent a factor that causes concern.

Various researches are being developed to observe the quality of resin composite polymerization with halogen based and LED based appliances (2, 12-14, 19, 30) Nevertheless, tests related to mechanical properties have shown that the halogen lamp appliances represent an important light source at present (14, 19, 22, 30, 34).

The degree of conversion of resin composites may be influenced by various factors. In this study, the shade of resin composite SL influenced the results and must be considered in clinical practice. The values obtained, expressed in percentages of monomer conversion, together with researches about the efficiency of light polymerizing appliances, offer dentistry an opportunity to conduct further research into clinical effect the residual monomers may have on the tooth.

It is important to point out that at present the LED based light sources represent a new technology, but in order to be adopted in dentists' offices, they must be further researched by the industries before being incorporated into clinical practice. The use of an extra-light resin composite such as, Charisma™ shade SL presents an option for direct restorations. Therefore, it does not require greater care, provided that halogen lamp equipment is used, and is constantly gauged, in order to offer adequate resin composite polymerization.

Conclusion

Based on the results obtained in this study, it may be concluded that:

1) Resin composite SL presented the highest degree of conversion, irrespective of the light polymerization time and the light source used.
2) Resin composite A2 required a light polymerization time of 20 and 40s with halogen light to obtain the same degree of conversion as that obtained by resin SL.

Conflict of interest disclosure

The author´s declared no conflict of interest in the present article.

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