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APPLICATION OF ESR SPECTROSCOPY IN THE STUDY OF THE LIGHT EFFICIENCY OF A DENTAL TRANSLUCENT FIBERGLASS POST TO PROMOTE POLYMERIZATION

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ESR spectroscopy allows for detection and quantification of free radicals (FRs) in a sample, which can be associated with the degree of monomer-to-polymer conversion (DC) of dental composites. This research seeks to probe the capacity of a translucent fiberglass post (TFP) to transmit light through its axis and promote polymerization by analyzing the amount of FRs in the sample as a function of the increasing length of a cylindrical TFP. A photopolymerizable dental composite resin was used to ensure that all FRs detected by ESR spectroscopy were generated by light-cure. The results revealed that the introduction of a 4 mm post decreased the DC by approximately 50% compared with irradiation in the absence of the post. In addition, increasing the length of the post dramatically reduced the amount of free radicals detected. This suggests that the TFP may have absorbed a large portion of the radiation, and the DC of resinous materials in the apical part of the root canal may be not sufficient to guarantee the fixation of the post.

Keywords: *electron paramagnetic resonance, degree of conversion, depth of cure, photopolymerization, dental composite resin.*

ПРИМЕНЕНИЕ ЭПР-СПЕКТРОСКОПИИ ПРИ ИССЛЕДОВАНИИ ЭФФЕКТИВНОСТИ ПРОПУСКАНИЯ СВЕТА СТОМАТОЛОГИЧЕСКИМ СТЕКЛОВОЛОКОННЫМ ШТИФТОМ ДЛЯ СТИМУЛИРОВАНИЯ ПОЛИМЕРИЗАЦИИ

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ЭПР-спектроскопия позволяет определять концентрацию свободных радикалов (СР), которые могут быть связаны со степенью конверсии (СК) мономеров в полимеры в стоматологических композитах. Исследована степень пропускания света вдоль оси стоматологического стекловолоконного штифта (ССШ), используемого для повышения эффективности полимеризации. С этой целью проведен анализ зависимости количества СР в образце от длины цилиндрического ССШ. Использована фотополимеризуемая зубная композитная смола, поэтому полагалось, что все СР, обнаруженные методом ЭПР-спектроскопии, получены в результате светового отверждения. Показано, что введение 4-мм ССШ уменьшает СК на ~50% по сравнению с облучением в его отсутствие. Увеличение длины ССШ резко сокращает количество обнаруженных СР. Это может означать, что ССШ поглотил большую часть излучения, и СК композита в верхней части корневого канала может быть недостаточной для гарантии фиксации штифта.

Ключевые слова: *электронный парамагнитный резонанс, степень конверсии, глубина отверждения, фотополимеризация, зубная композитная смола.*

Introduction. Intraradicular posts are indispensable when performing restorations in endodontically treated teeth to aid in the retention of the restorative material [1–6]. Due to their aesthetic properties, modulus of elasticity similar to dentin, low cost, and absence of corrosion, prefabricated fiberglass posts are frequently used to restore the lost part of a tooth [2, 3, 6–12].

Although cementing a fiberglass post is passive and retention is achieved through adhesion and friction [4, 13, 14], the discussion concerning the best adhesive system and resin cement that should be used to retain the post in the root canal continues [4, 15–18]. Resin cements that depend on the presence of light for complete conversion of monomers into polymers require that the post be capable of transmitting light to the middle and apical thirds of the root canal. If the degree of conversion (DC) does not achieve satisfactory values, unconverted monomers will affect the mechanical properties of the resinous material, i.e., the success of the restorative procedure [15, 18–21].

Fiber translucency and arrangement should ensure the post capacity for light conduction and the consequent polymerization of the cement throughout the length of the root canal. However, a few questions concerning the effectiveness of light transmission, the DC of the resin cement, the influence of the irradiation power, etc., remain unsolved. Because of this, resin cements are usually dual-cured, combining photo-cure and self-cure to guarantee that the portions of the resin cement will harden [22–31].

The polymerization of a dental material occurs by the addition of monomers in a chain reaction initiated by generating free radicals (FRs) [29, 30]. FRs are generated by the degradation of benzoyl peroxide, when the base paste is mixed to the catalyst (self-cure), and the absorption of the blue visible light by camphorquinone (light-cure). Some dental composites are dual-cured, combining these two initiation modes simultaneously. The DC is directly related to the amount of FRs generated at the initiation stage, so that the quantification of FRs is a reliable indirect measure of DC [29–31]. Since FRs are characterized by having unpaired electrons, electron spin resonance (ESR) spectroscopy can be used to detect and quantify the amount of FRs present in a dental resin sample [30–32].

In our previous works, we studied by ESR spectroscopy the influence of curing protocols [30] and geometrical configuration [31] on the depth of cure of a dual-cure resin cement indicated for cementing the post inside a root canal. For this, the amount of FRs generated in the cement mass surrounding the cemented post was analyzed. The double-shaped post light conduction capacity was significant for the first 8 mm and seemed to be nonexistent at the deepest points of the simulated root canal [30], while light conduction was more effective when a cylindrical post was used compared to a conical post [31]. However, some questions concerning the transmission of light through the TFP axis and the influence of the self-cure on the free radical signal remained unsolved. For example, for a dual-cured resin cement the self-cure starts when the base paste and the catalyst are mixed prior to cementation, so that when the sample is irradiated by the LED device, the polymerization reaction has already started. In addition, during data acquisition the self-cure reaction continues, so the FRs signal of the light-cured sample is not due to the photoinitiated reaction only.

This research was designed to probe the DC of a photopolymerizable composite resin positioned at the bottom of the post as a function of the increasing length of the TFP. A photopolymerizable composite was used instead of a dual-cure resin cement to ensure that all the radicals detected were generated by light irradiation, removing any influence of radicals generated by self-initiated reactions. As the sample mass was concentrated in a reservoir at the bottom of the post (not surrounding it), all the free radicals generated, and thus detected by ESR spectroscopy, were generated by the light conducted vertically through the TFP.

Experimental. *Experiment design.* The variables that can influence the number of FRs generated and thus the DC of dental resin cements or composite resins include the power of the curing device, irradiation time, post diameter, arrangement of the fibers, and cementation line thickness [30, 31]. In this experiment, the diameter of the post, the irradiation time (20 s), the irradiation power (1200 mW/cm^2), and the distance from the curing device to the cemented post were kept constant.

The material chosen for fabricating the matrices ensured that the curing light from the LED source would be transmitted through the post only. The cementation in the matrices was performed to stabilize the posts, with the apical portion flush with the lower face of the matrix, to avoid any possibility of light transmission through the post-matrix interface, and to make sure there was no interference in the experiment. In this study, supports for the composite resin samples were fabricated in order to standardize their dimensions. These supports were made with silicone, which does not produce an ESR signal and does not interfere in the data analysis.

The DC was assessed indirectly by measuring the amplitude of the FRs signal by ESR spectroscopy. The composite resin used was Filtek Z350XT (3M ESPE, Campinas, SP, Brazil), shade A2. The light source was a LED Optilight Max (Gnatus, RibeirãoPreto, SP, Brazil), with a 1200 mW/cm² potency. The TFP was White Post DC (FGM, Joinville, SC, Brazil) No. 3. To cement the post in the matrix, the dual-cure resin cement Allcem (FGM, Joinville, SC, Brazil), shade A1, was used. Both the composite resin and the TFP are commercialized worldwide and have qualities and properties very similar to other products on the market.

Obtaining posts and samples. A regular TFP is double-shaped. Its first 10 mm (from its cervical portion) is cylindrical in shape, and the other 10 mm conical in shape. In order to produce cylindrical posts, the TFPs were cut to obtain cylindrical TFPs (Fig. 1). The samples were divided into five groups of three samples each, with the following curing protocols: G+, positive control, with the samples being directly irradiated; G–, negative control, samples not irradiated; G4, light source 4 mm distant from the sample through the TFP; G6, as per G4 at 6 mm; and G8, as per G4 at 8 mm.

To hold the dental resin and ensure that all the samples had the same volume, small silicone tube samplers were fabricated, measuring 4 mm in external diameter, 2 mm in inner diameter, and 2 mm in height. The composite resin was inserted into the silicone tube with a metal spatula, so that the entire sampler volume was filled.

A base made of brass was fabricated, with a central hole (4 mm in diameter and 2 mm deep) to contain the silicone tube with the composite resin sample. Two guide pins (2 mm in diameter) were positioned laterally and equidistant to the central hole in order to guarantee the fixation of the matrices with the cemented post that would be coupled to the base. The external diameter (25 mm) and height (12 mm) of the base were adopted arbitrarily to guarantee safe handling of the sample and did not interfere in the experiment. The TFPs were sectioned using a double-sided fine-grain diamond disc (Microdont, Socorro, SP, Brazil) at a low speed.

The three matrices for guiding the TFP to the sample were made of brass with thicknesses of 2, 4, and 6 mm, respectively. The silicone tube with the resin sample inside it was inserted in the central hole of the base, and a thin polyester strip (10×10 mm) was positioned over the silicon tube to ensure that no contact occurred between the curing device or post and the resin.

The TFPs were cemented inside the matrices, leaving 2 mm of the post projecting above the matrix, as follows: the 4 mm post cemented in the 2 mm height matrix; the 6 mm post cemented in the 4 mm height matrix; and the 8 mm post cemented in the 6 mm height matrix.

Prior to cementation, the surface of the TFPs was cleaned with 70% alcohol and Prosil silane (FGM, Joinville, SC, Brazil). Disposable automixing points were used to mix the base paste and the catalyst in a 1:1 proportion by weight. The mixture was inserted into the central hole of the matrix, and the post was positioned inside it. Next, the composite resin was positioned in the silicone tube with the polyester strip over it inside the central hole of the base, the matrix with the TFP was coupled to the base, and the curing unit was activated for 20 s (Fig. 1) for G4, G6, and G8 samples. For G+, the samples were irradiated in the absence of the post, and for G–, the samples were not irradiated.

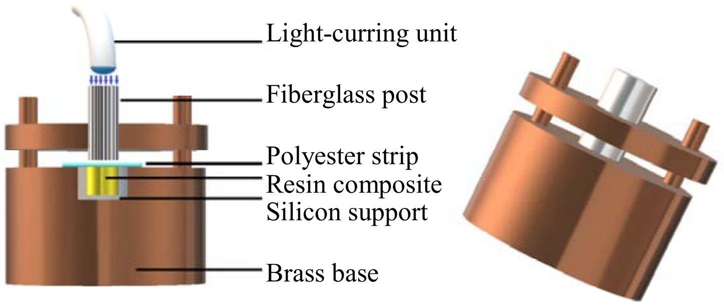

Fig. 1. Scheme of the final setup to obtain the polymerized sample of composite resin.

The ESR experiment. The polymerization of dental resins occurs in three stages. Initially, FRs are generated by the absorption of the blue visible light. Next, in the propagation stage, these FRs react with monomers, and the addition of monomers to the chain begins. Termination occurs when different active molecules combine to form a polymer. After generating FRs, the dental composite resin hardens rapidly, leaving a vitrified matrix. This vitrification traps the FRs in the sample due to the low mobility of monomers. Thus, the ESR signal of the FRs can be detected long after the initial irradiation [32].

Since the FR molecule possesses an unpaired electron, this molecule is paramagnetic, which means it is possible to evaluate the concentration of FRs of dental resins and resin cements by ESR spectroscopy.

In this study, the ESR spectrum was analyzed with regard to the signal amplitude to determine the concentration of FRs according to the length of the TFP. Since the signal amplitude of MgO:Mn^{2+} is constant and the signal of organic FRs is always located between its 3rd and 4th lines, it was used as an intensity standard and g marker. First, the MgO:Mn^{2+} spectrum was recorded (Fig. 2a). Next, each sample of the composite resin was inserted in the resonant cavity of the spectrometer, together with this g marker. Figure 3b shows the ESR spectrum obtained for G+, with the intensity standard. The 1st line of the FR superimposes with the 3rd line of MgO:Mn^{2+} (g = 1.978), but not with the 2nd line, so that it does not change its intensity. Thus, all the samples were modulated by this peak and had the same amplitude scale. The amplitude of the central peak was recorded for each sample (Fig. 2b) as a measure of the relative concentration of FRs, which in turn is directly related to the DC. The amplitude of the central peak (g = 1.949) was recorded for three samples from each group, and the average amplitude of the group was calculated.

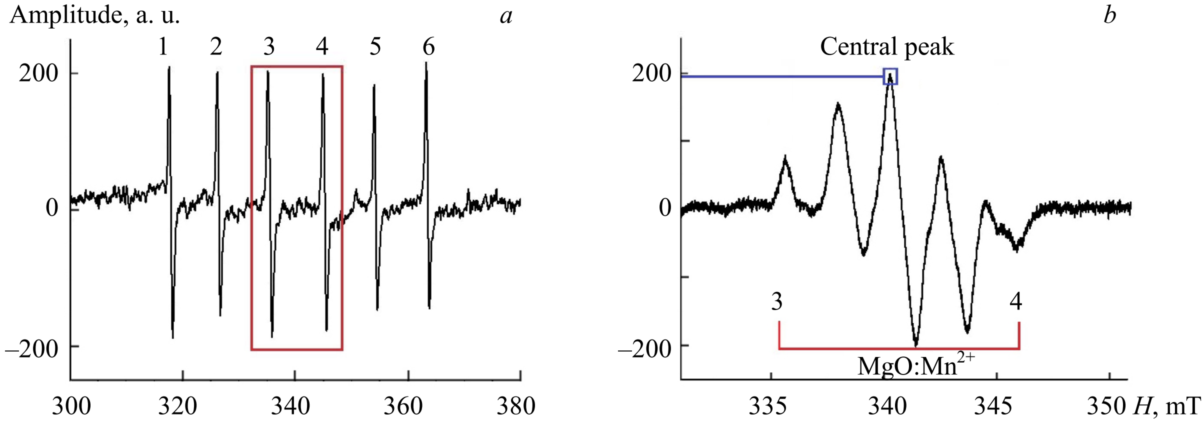

Fig. 2. The ESR spectra of MgO:Mn^{2+} (a) and FRs of the dental composite resin with the MgO:Mn^{2+} standard for G+ (b).

ESR spectra in the X-band (~9 GHz) were obtained using a JEOL (JES-PE-3X) spectrometer at room temperature, and the microwave power (1 mW), modulation amplitude (2 mT), and modulation frequency (100 KHz) were set to avoid signal saturation. A JEOL standard sample MgO:Mn^{2+} was used as an intensity standard and g marker. The samples of the composite resin from each group were inserted into quartz tubes and taken to the spectrometer immediately after irradiation. The data obtained were processed using Origin 8 (OriginLab).

In the [31–34], the characteristic signal of FRs of resin-based dental composites shows a 9 line spectrum with alternating intensities. In those cases, experiments were made with a modulation amplitude of ~1.0 mT. In this research, the modulation amplitude was set to 2.0 mT because of equipment limitations, resulting in five distinguishable ESR lines, as shown in Fig. 2b. The modulation amplitude affects the line shape but does not interfere in the data analysis and reliability of the experiment in this case because all the data were analyzed relatively to standard, positive and negative, controls.

Results and discussion. Analysis of the G-samples (Fig. 3a) clearly shows that no FRs are present without irradiation, while irradiating the sample directly, with no obstacle, produces a strong FR signal. The FR signal did not significantly change the amplitude of the 3rd line of MgO:Mn^{2+} (g = 1.978), so that this line was used to normalize the amplitude of all the samples tested (Fig. 3b). This also confirms that the methodology is a valid method of evaluating the DC of the composite resin. For each experimental group, the amplitude of the central peak was measured, and the average of this value was calculated and normalized with the amplitude of G+ (Fig. 4c).

The amplitude of G+ in relation to all the other groups (Fig. 3c) implies that even the shortest post (4 mm) did not produce a DC comparable with free irradiation. Where the curing light was transmitted through the post (G4, G6, and G8) to reach the sample, the DC decreased as the length of the TFP increased, indicating that the potency of the incident light on the composite resin sample decreased.

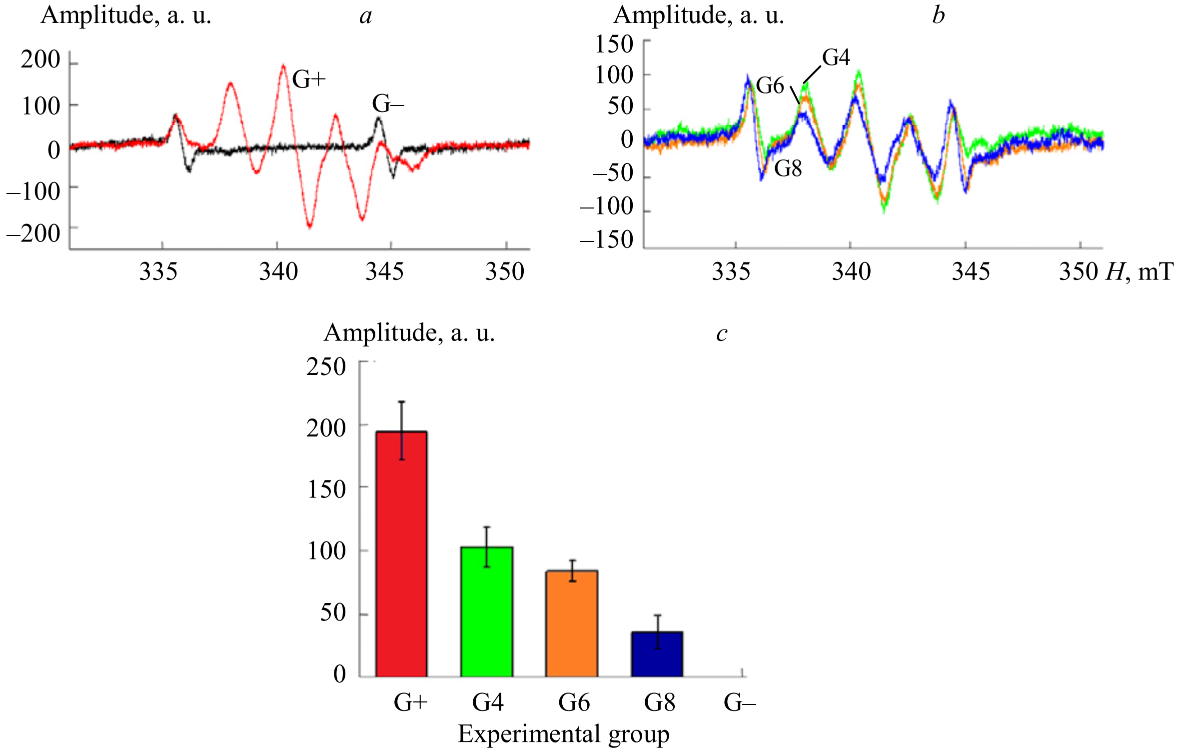

Fig. 3. X-band ESR spectra for (a) G+ and G–, (b) G4, G6, and G8, and (c) average amplitude of the central peak for G+, G4, G6, G8, and G–.

Fiber translucency and arrangement ensures the TFP capacity to conduct light, thus polymerizing the cement throughout the length of the root canal [20–28]. Clinically, the cementation procedure is subject to numerous variables, such as the quality of dentin, moisture, adhesion to the dentin system, and post composition [19, 13]. However, this research was designed so that the length of the TFP was the only variable. In this study, a light-cured restorative composite was used instead of the resin cement, because the DC of a dual-cure resin cement would be influenced by the chemical polymerization phase, masking the actual intensity of light capable of generating FRs. In addition, the study focused on the cylindrical portion of the post, which occupies the first third (closer to the light source) and the middle third of the root canal. It is important to keep in mind that in conical or double-shaped posts, a reduction in the area and disposition of glass fibers occurs, which further reduces the light intensity that can be conducted through the length of the post [31].

Analysis verified that the introduction of the smallest post reduced the DC by approximately 50% of that observed when the incident light had a free path to the sample (Fig. 3c). Where the TFP was present, a reduction of approximately 20% in the DC was verified between G4 and G6, a 2 mm increase, while between G4 and G8, a 4 mm increase, the reduction in the DC was ≈65%. These results are critical since this commercial TFP is 20 mm in length, and its geometrical configuration varies along its length. These findings suggest that in a clinical application, the deep part of the restoration may not be polymerized if the retentive system is only photo-activated. This suggests that the TFP may have absorbed a large portion of the radiation and is not capable of influencing the DC of the resinous material in the apical part of the root canal.

The findings in this research are in agreement with the results from [19, 22–25], showing that increases in the length of the TFP and the distance from the light source corresponded to decreases in the DC of the photopolymerizable composite used in their respective experiments. In this respect, the electron spin resonance technique is shown to be adequate to probe the polymerization of dental composites.

Conclusion. The results demonstrate that increasing the length of the post dramatically reduces the amount of free radicals generated. From the clinical point of view, an alternative curing protocol (as the initiation by degradation of benzoyl peroxide in the self-cure) is always necessary to guarantee retention of the fiber post inside the root canal and must be used in conjunction with the light-cure.

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