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Effect of the Incorporation of EDB Co-initiator in the Resin in Halogen and LED Light

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This paper evaluated the influence of the incorporation of the coinitiator Ethyl 4-(dimethylamino) benzoate (EDB) in Filtek Z250 XT resin in the reduction of the polymerization time and its behavior in halogen light and LED (Light Emitting Diode) light. The samples were subjected to thermal and spectroscopic analysis. The TG/DTG-DTA curve showed that both samples studied have a thermal stability temperature similar to the other polymers in the monomer blend. Morphological features were analyzed by SEM. By the MIR analysis, the degree of conversion using halogen light showed a better result compared to the LED light. The polymerization time applied to the specimens was 10 seconds, reducing the original resin time by half.

Keywords: *Composite Resins, Polymerization, Dental Restoration.*

1. Introduction

Developed by Raphael L. Bowen, composite resins have gained significant prominence for their advancement in restoration technique and for their physical and esthetic properties. Nowadays, composites are still studied to obtain improvements, such as reduction of polymerization time, and better mechanical properties[1]. The inorganic filler is the largest compound in composite resins (70 wt.%). The organic matrix has two or more organic monomers, which is approximately 26 wt.% of the total formulation. The remaining 4% in its composition is represented by photoinitiators, pigments and thinners[2,3]. Filtek Z250 XT resin has more than 70% of inorganic filler in its composition (Table 1). This filler is used to simulate as closely as possible the human tooth after light curing[5]. The monomers used in the resin are TEGDMA, UDMA, Bis-GMA and Bis-EMA (Figure 1), they are currently the most used monomers for this purpose[6].

The photoinitiator and coinitiator are present in the composite resin. The photoinitiator absorbs light and interacts with the coinitiator, then, producing free radicals that are responsible for the polymerization process[7-9]. Camphorquinone is the most used photoinitiator, it has a maximum wavelength absorption at 470 nm[10]. The coinitiators that present greater reactivity are tertiary amines such as Ethyl 4-(dimethylamino)benzoate (EDB), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and *N*-methyl-*N*-ethylcyanamide (CEMA)[11,12].

The polymerization of the restorative material, when performed correctly exhibits a surface smoothness, appropriate anatomical shape, ideal mechanical properties and longevity; these aspects are related to a success in restoration process[13,14]. Therefore, to activate the photoinitiator, a light-curing equipment is used[15]. The halogen light curing device is one of the most used equipment, which is considered a convenient alternative method compared to other devices[16,17]. Another light curing device used is the LED (Light Emitting Diode) that normally has a wavelength range in the blue region (450-490 nm); however, other regions can be used, depending on the selected photoinitiator[18].

In a dental office, several patients are treated, including people with some disability such as mental and physical limitations, autism spectrum, the elderly people, who are unable to sit, or to maintain their mouth open for a long period and are often subjected to various dental procedures. The polymerization time is often equal or superior to 20 seconds. It is important to continuously improve these restorative materials, to enhance their effectiveness rate, and to reduce the polymerization time, then, supporting the patient comfort. The objective of this work is to evaluate the influence of the incorporation of the Ethyl 4-(dimethylamino) benzoate (EDB) as co-initiator in Filtek Z250 XT resin to reduce the polymerization time under halogen light and LED (Light Emitting Diode) sources. The final polymers were further analyzed by simultaneous thermogravimetry-differential thermal analysis (TG-DTA) and scanning electron microscopy (SEM) to evaluate their thermal behaviour and morphological features.

2. Material and Method

2.1. Photopolymerization

The samples were made with the restorative composite Filtek Z250 XT composite resin (3M ESPE St. Paul, Mn,

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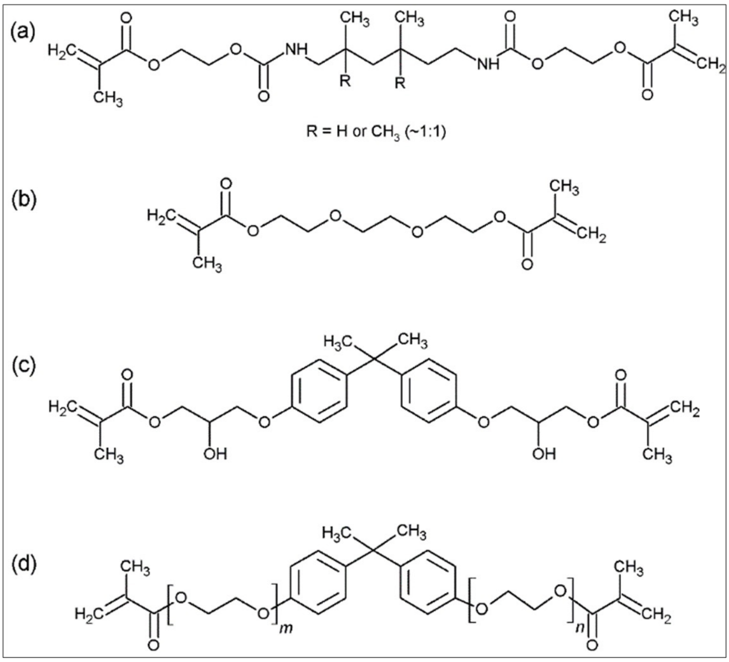

Figure 1. Chemical structure of the monomers used in Filtek Z250 XT: UDMA (a), TEGDMA (b), Bis-GMA (c) and Bis- EMA (d).

Table 1. Composition of Filtek Z250 XT resin.

Constituent*	No. CAS	Wt.%
Treated silanized ceramics	444758-998-9	70 – 85
Bisphenol A diglycidyl ether dimetacrylate (BisGMA)	1565-94-2	1 - 10
Bisphenol A polyethylene glycol diether dimethacrylate	41637-38-1	1 – 10
Dimethacrylate diurethane (UDMA)	72869-86-4	1 -10
Silane treated silica	248596-91-0	1 – 10
Triethylene glycol dimethacrylate (TEGDMA)	109-16-0	<1

3M- Chemicals Safety Information Sheet. 2020[4].

USA) together with EDB co-initiator, using Halogen light (Light-cured light apparatus Halogen - CLK-50 Kondortech São Carlos-SP, Brazil) and LED light (VALO Ultradent® LED Light Curing Apparatus, USA). The EDB was macerated and added in the composite resin (0.1 Wt.%). Therefore, the EDB and composite resin were blended in a polypropylene container. Each sample was synthesized in a black Teflon matrix- kit-type with a central hole (10 mm in diameter and 2 mm in depth). The material was compressed with a static load of 1 kgf inserted on a glass slide interposed by a polyester strip; this process was performed to remove the excess of material and to leave the composite surface level with the edge of the matrix side wall. After removing the weight, the glass slide and the polyester strip, these samples were light-cured using a CLK-50 light-curing device (Kondortech®, São Carlos), which has a halogen lamp (400-550 nm, irradiance of 600 mW/cm^2). The other sample was cured using a VALO broad-spectrum light-curing device (Ultradent®, USA) with a continuous light (430–490 nm, irradiance of 1000 mW/cm^2) LED lamp. Both were submitted to an initial cure time of 10 seconds, which is the minimum time set for the light curing equipment and we observed the hardening of the sample.

2.2. Characterization thermogravimetry - differential thermal analysis (TG-DTA)

Thermal stability, decomposition steps, events involved in these steps, as well as the amount of inorganic material were obtained by TG-DTA curves. The TG-DTA curves of the monomeric mixture (Filtek Z250 XT) as well as the polymers (from the halogen lamp and LED) were obtained using the equipment STA Jupiter 449 F3 (Netzsch). Using 70 µL α-alumina crucibles with sample masses close to 28 mg and heating rate of 10 °C min^{-1} in dry air atmosphere with a flow rate of 70 mL min^{-1} in the temperature range of 30.0 to 800.0 °C.

2.3. Mid-Infrared spectroscopy (MIR)

The spectra in the Mid-Infrared region of the composite resin, polymer synthesized under halogen lamp and under LED lamp were obtained using a Vertex 70 spectrophotometer (Bruker) through the attenuated total reflectance method with scanning range between 1560 and 1680 cm^{-1} (resolution of 4 cm^{-1}) using the diamond crystal as support. The monomer conversion (MC) was calculated using the absorbance area of carbon–carbon double bonds (C=C) at 1637 cm^{-1}. The MC was calculated following the Equation 1.

$$MC(\%) = (1 - \frac{Polymer\ absorbance\ area}{monomer\ absorbance\ area})*100 \qquad (1)$$

2.4. UV-vis spectroscopy in solid state

In solid UV-vis spectroscopy analysis the absorption and transmittance spectra in were captured using thin films (5 mm) of each polymer, in a Perkin Elmer Lambda 1050 double-beam spectrophotometer measured with wavelength between 250 and 850 nm.

2.5. Scanning electron microscopy (SEM)

Polymer morphology was studied using an EVO LS15 scanning electronic microscope from Zeiss. Samples were macerated into small pieces, placed over a SEM standard carbon adhesive and plated with gold. The voltage was set at 15 kV and samples were analyzed, in a high vacuum environment (10^{-3} Pa), at ×500 magnification.

3. Result and Discussion

3.1. Thermogravimetry analysis - differential thermal analysis (TG-DTA)

Thermal stability for UDMA, TEGDMA, Bis-GMA and Bis-EMA polymers can be found in the literature as 213.8°C; 132.6°C; 227.6 °C and 165.2°C; respectively[19]. These are used in the commercial monomer mixture (Filtek Z250 XT). Table 2 exhibits details of temperature of thermal events, percentage of mass loss and peak temperature (DTA) related to each sample. The TG/DTG-DTA curve for the monomer mixture is displayed in Figure 2a. The first mass loss is related to the evaporation of the solvent, ethanol present in the sample. The monomeric mixture is stable up to 208.1 ºC. Above this temperature, the monomeric structures are thermally degraded (decomposed) in two steps of mass loss. Note that the second mass loss step refers to thermal degradation (208.1 - 467.9 ºC) and it is a degradation with several consecutive and overlapping steps (at least 3 events) as shown in the DTG curve (complex decomposition). The third stage of mass loss refers to the degradation and oxidation of the carbonaceous matter. Finally, the residue for the sample was 75.45%. The polymer synthesized by halogen lamp (P-halogen, Figure 2b) has a TG curve similar to monomeric mixture; however, the P-Halogen polymer has a thermal stability slightly superior (213.7 °C). It is observed the vaporization step (30-213.7 ºC), followed by the first degradation step (213.7-468.0 ºC), which is also complex and has two consecutive and overlapped events. The last mass loss step is related to oxidation and degradation to the degraded and carbonaceous polymeric structure. At the end of the analysis there is a residue of 75.42%. The polymer synthesized with the LED (Figure 2c) has a profile similar to P-Halogen with a thermal stability up to 214.6 ºC. Decomposition takes place in two stages, the first being a complex thermal decomposition and the second the oxidation and degradation of the carbonaceous material. The residue found was 75.71%.

Both materials studied have a temperature of thermal stability similar to other polymers of monomeric blends (UDMA, TEGDMA, Bis-GMA and Bis-EMA) found in the literature[20]. From the inorganic material residue, it was possible to calculate an average number equal to 75.53 ± 0.16%; this value is within the range established by the manufacturer which is between 70% to 85%. The thermal stability, maximum

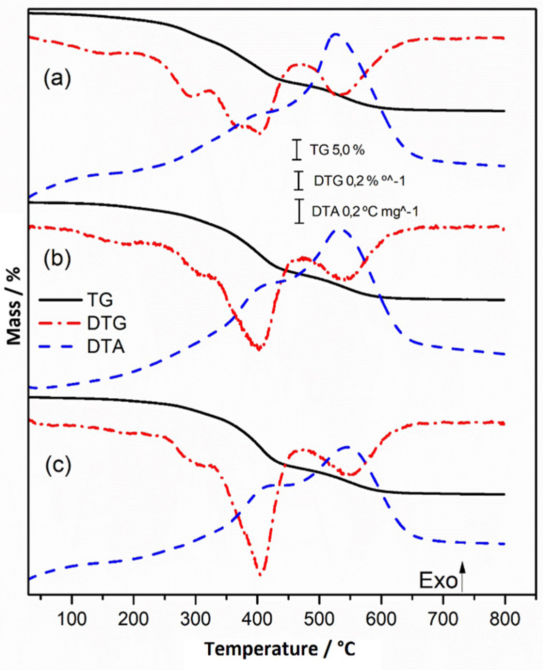

Figure 2. TG/DTG-DTA curves for the monomeric mixture (a), P-Halogen (b), P-LED (c).

Table 2. Temperature of thermal events (θ°C), loss of mass (Δm) and peak temperature (T_p) observed in each TG-DTA curve for UDMA system samples.

Volatilization and thermal decomposition steps					
Samples		Volatilization step	1st decomposition	2nd decomposition	Residue (%)
Monomeric mixture	θ °C	30.0-208.1	208.1-467.9	467.9-662.8	75.45
	Δm /%	1.73	16.26	6.56	
	Tp/°C	-	353.0-438.7*	526.6↑	
Polymer- Halogen	θ °C	30.0-213.7	213.7-468.0	468.0-656.2	75.42
	Δm /%	2.40	15.88	6.30	
	Tp/°C	-	401.2↑	531.6↑	
Polymer – LED	θ °C	30.0-214.6	214.6-465.8	465.8-656.1	75.71
	Δm /%	1.61	16.23	6.45	
	Tp /°C	-	410.3↑	545.9↑	

*exotherm; ↑peak exo

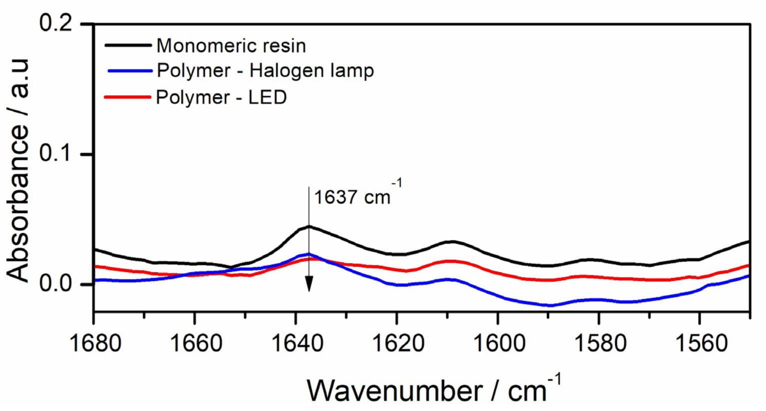

Figure 3. MIR spectra for the monomeric system and polymers.

temperature at which a given sample reaches before being degraded, did not show significant changes in this analysis between samples, it can be noted that the EDB coinitiator present in the materials did not affect the thermal events.

3.2. Mid-infrared spectroscopy (MIR)

The conversion of individual monomers using camphorquinone and LED (430-470 nm) after 400 seconds of light absorption is 75.83% for UDMA; 79.80% for TEGDMA; 51.38% for Bis-GMA; and 34.37% for Bis-EMA[21]. It is observed that the highest conversions are found for UDMA and TEGDMA; thus, monomeric mixtures could reach a conversion between 50-80%. The band at 1637 cm^{-1} referring to the C=C stretch of the methacrylate group (Figure 3) it is noted that the absorption of this band is higher in the monomeric resin and lower in the polymers, this is expected due to the consumption of the double bond in the reaction of polymerization, thus decreasing the concentration of C=C in the system. For the monomer conversion (MC), the area of the band at 1637 cm^{-1} was used. From the spectra and using Equation 1 it was possible to calculate the total conversion for the polymers with the two light sources after 10 seconds of light irradiation. It is observed that halogen light had a lower conversion (50.33%) when compared to LED (60.28%) – Figure 4. This result shows that the use of LED has increased the conversion of the polymer.

The performance of polymerization in composite resin depends on hue, resin composition, thickness, diameter of the light curing equipment tip, position, light intensity, wavelength, and exposure time[22,23].

Some LED light curing equipments can emit light greater than 1000 mW/cm^2, which replaces the halogen lamp without affecting the polymerization process. The intensity of LED light influences the light exposure time in the polymerization process, reducing polymerization time and obtaining a better conversion[15,24]. This fact was observed in the present work.

The photoinitiator has a specific light absorption range. The type of photoinitiator used in composite resin influences the choice of light. Therefore, it is important to know the wavelength range and light intensity emitted by light source equipment[25,26].

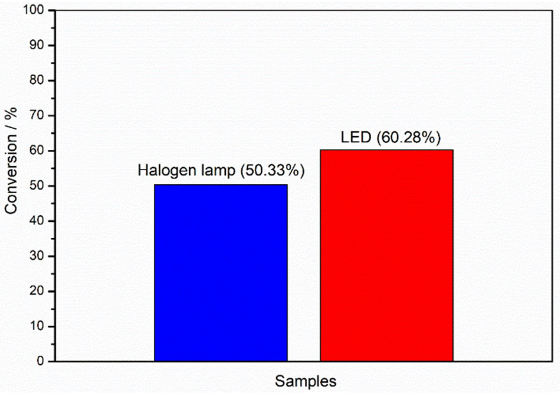

Figure 4. MC (%) values for each sample after 10 s of exposure.

Although halogen light curing equipment covers a long wavelength from 400 nm to 600 nm, the wavelength that camphorquinone absorbs is 470 nm. LED light has a narrow emission spectrum within the absorption range of camphorquinone, which makes LED light more efficient and without an overheating process[27-29].

In Ceballos et al.[24] found that an exposure time of 20 seconds via LED light had a statistically higher hardness value than halogen light. Same result was found after 40 seconds. Concluding that LED light provides a decrease in the exposure time with better physical results. Another study[18,30] reported that LED exhibited a better performance when LED and Halogen equipments emit 100 mw/cm^2. Mills et al. compared a LED equipment and a Halogen equipment emitting 300 mW/cm^2; the LED equipment had a better result in depth of polymerization in the specimens than the halogen light[26]. Briso and coauthors compared four different light sources, where three consisted with LED (140 mw/cm^2 , 200 mw/cm^2 , 400 mw/cm^2) and one halogen light equipment (380 mw/cm^2); the Elipar Freelight equipment performed better than the others due to its higher intensity (400 mw/cm^2). It demonstrated higher microhardness values compared to halogen light, justified by the wavelength radiated by LED light, which is in agreement with the absorption of camphorquinone[25].

In the present work, the light intensity in the light curing equipment is different, with 1000 mW/cm^2 for LED light against 600 mw/cm^2 for halogen light. From the results and according to the authors above, it can be stated that the high light intensity increased the degree of conversion. Another point is the wavelength of the LED light that corresponds to the same absorption peak of the photoinitiator (camphorquinone), allowing a greater effectiveness in the polymerization process (Figure 4).

3.3. UV-vis spectroscopy in solid state

The spectra were analyzed by transmittance in the range between 250 and 850 nm. The high inorganic load of the resin (>70%) makes the UV-Vis absorption spectra of the solids obtained not so concise. Therefore, we performed the study of UV-vis spectra to see differences between the materials and reproduce the natural tooth shade aiming esthetic restorations with natural appearance. However, it is possible to observe the same profile of the curves (Figure 5). As observed in the transmittance spectra, we do not have a high percentage of material transmittance, this is seen in the opacity of the samples.

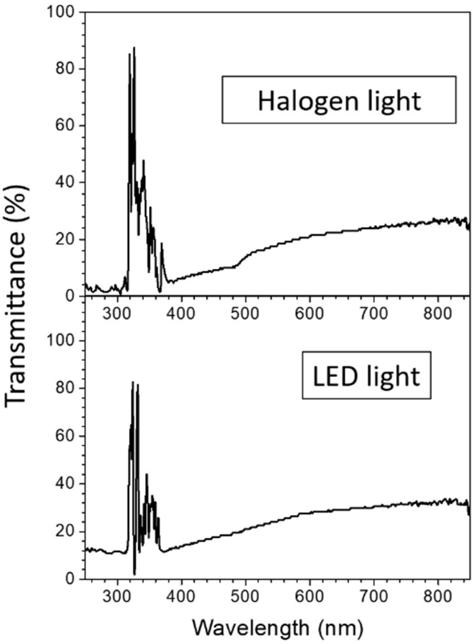

Figure 5. UV-vis spectra of each polymeric sample.

In the 3M – Chemicals Safety Information Sheet[4] we can see the presence of crystalline silica and silicon dioxide. Silicon is an indirect band semiconductor, so there is low transmittance to longer wavelengths (above 400 nm) that can be attributed to this compound[31,32]. We can also observe a slight band around 500 nm in both samples, which can be attributed to SiO_2 [33]. The intense bands below 300 nm can also be originated from the bonds contained in the methacrylic structures (e.g. the π-π transitions *, σ-σ*, n-σ* and n-π*). As inorganic fillers (ex. SiO_2 and $CaCO_3$) inserted in this type of resin do not emit fluorescence, this technique can show information collected from methacrylic coatings (UDMA, TEGDMA, Bis-GMA and Bis-EMA) spread on the inorganic substrates.

3.4. Scanning electron microscopy (SEM)

In the SEM images (Figure 6) both polymers exhibit cleavage fractures after the maceration process. This type of fracture indicates that the material is solid and tough, which validates a successful polymerization process in only 10 seconds. Furthermore, holes from the solvent are not observed and the filler material is homogeneous in whole sample.

3.5. Light curing with halogen light and LED light

The minimum activation time of the halogen light curing device as the LED light curing device used in this work is 10 seconds. The samples from both groups were initially subjected to the minimum time of light incidence and it was observed that the polymerization occurred with sample hardening. The resin used Filtek Z250 XT takes 20 seconds to light cure as suggested by the manufacturer. In this study, the EDB coinitiator in association with the resin potentiated the activation, provided acceleration in the polymerization process, reducing this time by half.

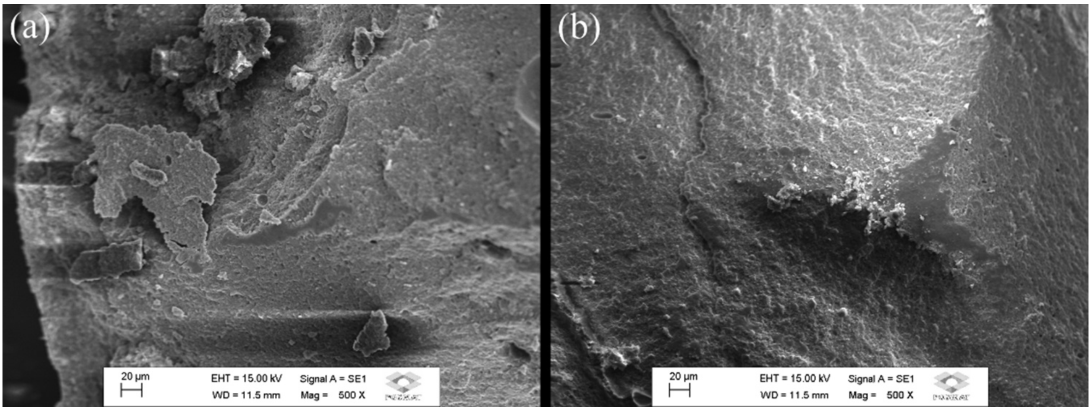

Figure 6. SEM images for P-Halogen (a) and P-LED (b).

4. Concluison

Based on the methodology used and the results obtained, it was observed that the incorporation of EDB coinitiator (0.1 Wt.%) did not change the physicochemical properties of the Filtek Z250 XT composite resin and the polymerization time was reduced by half. As well as the use of LED light allowed greater total conversion to polymers when compared to halogen light.

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