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Degree of Conversion of Z250 Composite Determined by Fourier Transform Infrared Spectroscopy: Comparison of Techniques, Storage Periods and Photo-activation Methods

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The purpose of this study was to evaluate the degree of conversion (DC) of the Z250 composite, using six photo-activation methods, two storage periods and two preparation techniques of the FTIR specimens (n = 3). For the KBr pellet technique, the composite was placed into a metallic mold and photo-activated as follows: continuous light, exponential light, intermittent light, stepped light, PAC and LED. The measurements were made after 24 h and 20 days. For the resin film technique, approximately 0.07 g of the composite was pressed between two polyester strips, photo-activated as above described and analyzed. The DC was calculated by the standard technique and submitted to ANOVA and Tukey's test ($\alpha = 5\%$). Independently of the storage period and specimen preparation technique, there were no significant differences among photo-activation methods. No statistical difference was observed between the time periods used. The specimens analyzed under the KBr pellet technique presented higher DC values than those analyzed by the resin film technique.

Keywords*: dental materials, composite resin, degree of conversion, FTIR, photo-activation methods, depth of cure*

1. Introduction

Restorative composite resins are composed by a resinous matrix (organic phase), in which silanizated fillers are dispersed. This matrix is typically a mixture of at least two dimethacrylate monomers. In general, one of the monomers is relatively viscous, nominated as base monomer, whilst the other one presents a low viscosity, the diluent monomer. The dimethacrylates frequently employed as base monomers in Dentistry are Bis-GMA and UDMA, as a diluent monomer is used TEGDMA. This combination results in a material with good handling properties.

The base monomers decrease polymerization shrinkage due to their relatively large molecular volume and, in the case of Bis-GMA, the stiffness of the molecule results in increased elastic modulus of the polymer. Conversely, the diluent monomer improves copolymer conversion due to its greater flexibility, lower molecular volume and lower viscosity, which provides greater mobility to the system[1,2].

With regard to the light cured composites, the final properties of the material depend upon light curing, which difficult the description of the ideal curing method. Although optimization of the mechanical and physical properties of a composite is desirable, it is important to minimize polymerization shrinkage, in order to preserve the tooth/restoration interface integrity[3,4].

Some researchers have found better integrity of the bond to the cavity wall of a tooth when the cure rate is reduced[3]. This finding was suggested to be due to an increased ability to flow, providing partial relaxation of polymerization shrinkage[5]. A significant problem that arises when using low intensities is lower degree of conversion (DC) and a reduced curing depth[6,7]. Thus, longer curing times[7-9] or post curing at higher intensity[10-12] can compensate this problem.

Several technologies have been suggested to initiate the polymerization reaction. The halogen lamp with a high in-

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tensity is the most common and well known[6,9]. Some variations in technique may be performed in an attempt to reduce polymerization shrinkage, whilst maintaining the DC. Such variations include stepped light[10-13], exponential light[14] and intermittent light[12]. Another method employs the plasma arc curing (PAC) lamps, which provide a high intensity in a short time[15]. Finally, the light emitting diode (LED) can also be used to initiate the photo-activation process in the composite resin[16,17].

Irrespective of the photo-activation method, the DC should be higher as possible. However, Bis-GMA and UDMA based dental composites exhibit incomplete conversion of double bonds, ranging between 43-85 %[13,15,18-21], due to the complex reaction mechanism.

FTIR spectroscopy has been extensively used to determine the DC of dental composites[18,20-24]. However, the techniques for FTIR analysis and the time periods required after specimen preparation are not well established. The literature reports two techniques for FTIR analysis: potassium bromide (KBr) pellet[18,20] and thin resin films[15,20-24]. Time periods reported can range from immediately after specimen preparation to up to some days[18,20-24].

The purpose of this study was to evaluate the DC of the Z250 composite resin, using six photo-activation methods (continuous light, exponential light, intermittent light, stepped light, PAC And LED), two time periods (24 h and 20 days), and two preparation techniques of the FTIR specimens (Potassium Bromide [KBr] pellet and thin resin film).

2. Materials and Methods

The present study used the Z250 composite resin, shade A3 (3M, St. Paul, MN, USA). Composition and batch number are listed in Table 1. The samples to be analyzed by FTIR spectroscopy were prepared by two techniques: potassium bromide (KBr) pellet and thin resin films. Concerning about KBr pellet technique, the FTIR analysis was performed with specimens submitted to two storage periods: 24 h and 20 days.

For the KBr pellet technique, 0.11 g of the composite was placed in a circular brass matrix of 6 mm in diameter and 2 mm in height. The composite was then covered with a polyester strip and pressed with a glass slab to accommodate the material into the matrix. Photo-activation was performed as it follows: a) continuous light; b) exponential light; c) intermittent light; d) stepped light; e) PAC, or; f) LED. For the continuous light photo-activation method, the curing tip was positioned close to the brass matrix/restorative composite. The photo-activation was performed for 40 s with a light intensity of 800 mW/cm^2, using Elipar Trilight curing unit (3M-ESPE, Seefeld, Germany). For the exponential light technique, the same curing unit was used, however, the light intensity began at zero, increasing gradually to 800 mW/cm^2, with a total exposure time of 40 s. Curing with the intermittent light method was performed using a device made in the Dental Materials Department, Dental School of Piracicaba, UNICAMP, which provided 2 s of light with intensity of 600 mW/cm^2 and 2 s without light. The total exposure time was 80 s. The stepped light method was performed using a XL 2500 curing unit (3M-ESPE, Seefeld, Germany), which provided an initial 10-second exposure of the activating light with an intensity of approximately 150 mW/cm^2, maintaining a distance of nearly 2.0 cm to the specimen. The curing tip was then positioned close to the brass matrix/restorative composite, resulting in an increased light intensity of 650 mW/cm^2, which was maintained for additional 30 s. For the PAC technique, the Apollo 95 E curing unit was used (DMD, Westlake, Village, CA, USA) which, according to manufacturer's information, achieved an intensity of 1320 mW/cm^2. The exposure time was 3 s. Finally, for the LED method, a LEC 470 l curing unit (M M Optics, São Carlos - SP, Brazil) was used to photoactivate the composite, providing an intensity of 100 mW/cm^2 for 40 s. The light intensity of the curing units was measured with a radiometer (Curing Radiometer, model 100, Demetron/Kerr, Danbury, CT, USA), with the exception of the Apollo 95 E curing unit.

After photo-activation, the polymerized composite resin was pulverized into fine powder with a hard tissue-grinding machine (Marconi, model MA590, Piracicaba - SP, Brazil). The pulverized composite was maintained in a dark room until the moment of the FTIR analyzes. Ten milligrams of the ground powder was thoroughly mixed with one hundred milligrams of KBr powder salt. This mixture was placed into a pelleting device (Aldrich, Milwaukee, WI, USA) and then pressed in a hydraulic press (Carver Laboratory Press, model 3648, Wabash, St. Morris, USA) with a

Table 1. Composition of organic matrix and filler of the Z250 composite resin.

Organic Matrix	Filler Type	Filler vol (%)	Filler Size (μm)	Batch
Bisphenol A diglycidyl ether dimethacrylate (BisGMA), urethane dimethacrylate (UDMA) and Bisphenol A polyethylene glycol diether dimethacrylate (BisEMA). Camphoroquinone (initiator)	Zirconia/silica	60	0.19-3	1NL 2004-08.3

load of eight tons, to obtain a pellet. This pellet was then placed into a holder attachment into the spectrophotometer (Bomem, model MB-102, Quebec - Canada) for analysis. For this technique, the specimens were made and analyzed after two storage periods: 24 h and 20 days.

For the thin resin film technique, approximately 0.07 g of the composite was placed between two polyester strips and pressed with two plain glass slides, on either side of the material. The thin resin film (60-70 μm) was photo-activated according to the same methods as described before. After 24 ± 1 h, the thin films were separated from the polyester strips and analyzed by the FTIR spectrophotometer. The uncured composite resin was analyzed using a metallic siliceous window. The measurements were recorded in absorbance, with a FTIR spectrometer (Bomem, model MB-102, Quebec, Canada) operating under the following conditions: 300-4000 cm^{-1} wavelength; 4 cm^{-1} resolution; 32 scans. The percentage of unreacted carbon-carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm^{-1}) against internal standard before and after curing of the specimen: aromatic C···C (peak at 1610 cm^{-1}) and urethane N···H (peak at 1537 cm^{-1}). The degree of conversion was determined by subtracting the % C=C from 100%. All experiments were carried out in triplicate. The data were analyzed by ANOVA and the means were compared by Tukey's test (5% of significance level).

3. Results and Discussion

According to the results presented in Tables 2 and 3, all photo-activation methods showed no statistical difference among themselves ($p > 0.05$) for DC values, inspective of the FTIR technique and period of storage. These results indicate that all tested methods were able to appropriately cure Z250 composite, despite the differences (e.g. energy density) among them. Several factors may be responsible for such a similarity among the photo-activation methods, including spectral distribution of the light emitted by the curing unit, the polymerization process itself and the nature of the monomer system.

The energy density is the product of the output of the curing unit (in mW/cm^2) and the time of irradiation (in seconds), and is an important parameter of the curing unit[4,15,25], keeping the distance between the curing tip and the specimen surface constant. On this study, the energy densities of the tested photo-activation methods varied greatly, ranging between 3.96 and 32 J/cm^2. However, this variation did not affect the DC values of the specimens tested. Variations in DC may be the consequence of other factors that affect the conversion of the material (spectral distribution of light, the polymerization reaction itself and monomer system), as well as the variations in the property measurements of the output of the curing unit obtained. Mills *et al.*[26] showed that the output of the curing unit differs greatly when it is measured using a commercial dental radiometer designed for office use or when measured with a power meter, which shows the distribution of the light output across the spectrum. Differences also exist among commercial radiometers and these measurement variations result in different density energies. In this study, it was employed a headpiece radiometer to obtain the light intensity.

Camphoroquinone presents an absorption peak at a wavelength of 468 nm. Hence, the closer the curing unit is wavelength to this absorption peak, the greater its ability to activate camphoroquinone and, thus, to initiate the polymerization process. Although LED devices usually achieve lower light intensity (and lower energy density) than halogen curing units, the wavelength peak of the LED curing unit is 466 nm[16], i.e. very close to the camphoroquinone absorption peak. According to Nemoto[27], the narrow wavelength spectrum emitted by LED devices lies within the 450-490 nm range, a range which appropriately polymer-

Table 2. Means of DC according to analyzed periods and photo-activation methods, for the KBr pellet technique.

Photo-activation method	DC after 24 h (%)	DC after 20 days (%)
Continuous light	66.25 (2.55) a A	62.64 (1.98) a A
Intermittent light	63.74 (2.37) a A	59.14 (5.24) a A
Stepped light	62.94 (4.92) a A	62.17 (6.26) a A
LED	62.14 (10.15) a A	58.05 (3.50) a A
PAC	60.01 (1.13) a A	59.64 (2.14) a A
Exponential light	59.61 (5.85) a A	60.37 (1.79) a A

Means followed by distinct small letters are statistically different in columns ($p < 0.05$), by Tukey's test.
Means followed by distinct capital letters are statistically different in lines ($p < 0.05$), by Tukey's test.
( ) Standard deviation.

Table 3. Means of DC according to FTIR technique analyzed and photo-activation methods used (24 h).

Photo-activation method	KBr pellet (%)	Thin film (%)
Continuous light	66.25 (2.55) a A	52.84 (4.32) a B
Intermittent light	63.74 (2.37) a A	46.90 (2.41) a B
Stepped light	62.94 (4.92) a A	59.50 (2.30) a B
LED	62.14 (10.15) a A	51.07 (4.23) a B
PAC	60.01 (1.13) a A	49.70 (4.23) a B
Exponential light	59.61 (5.85) a A	47.89 (3.67) a B

Means followed by distinct small letters are statistically different in columns ($p < 0.05$), by Tukey's test.
Means followed by distinct capital letters are statistically different in lines ($p < 0.05$), by Tukey's test.
( ) Standard deviation.

izes the composites that use camphoroquinone as initiator. Thus, the LED light curing device achieves an almost ideal light source emission.

PAC units are characterized by a very high output (approximately 1320 mW/cm^2, according to manufacturer's information) in a rather narrow range of wavelengths around 470 nm, however, the exposure time is just a few seconds. This results in lower energy density, however the peak absorption wavelength is near to that of camphoroquinone.

Although the LED and PAC curing units provided the lowest energy densities (4 J/cm^2 and 3.96 J/cm^2, respectively), the DC values were not statistically different to halogen light sources. This finding may be explained by the wavelength peak at approximately 468 nm, emitted by these curing units, which activates camphoroquinone more efficiently. The halogen curing units exhibit higher energy density, however, they also present a wide wavelength range of between 380-510 nm, with a wavelength peak at 484 nm[16]. The halogen lamps generate heat, becoming extremely hot (near to 400 °C), resulting in a 70% loss of output. However, the light intensity decreases to 10% when a cut-off filter is used to obtain the optimal wavelength range required for curing composite resins. Thus, the final ratio of available wavelength range for the polymerization process is only 1% of the total energy output of the halogen lamps[16]. Despite these variations in curing units and photo-activation methods, no significant differences in DC values were observed, as mentioned before.

The cross-linked nature of the composite resins makes the photo-polymerization of the dimethacrylate monomers a complex process. Different behaviors are exhibited during the reaction, such as autoacceleration, autodeceleration, termination processes controlled by reaction diffusion, formation of structural heterogeneities (microgels) and limiting functional groups conversion. Firstly, monomer molecules are incorporated into chains as units containing pendent bonds. Further propagation can proceed by addition of the next molecule (growing polymeric chain), by an intramolecular attack of the radical site on the pendent double bond (primary cyclization) or by an intermolecular linkage (cross-linking) that leads to network formation. The apparent reactivity of pendent double bonds on the same chain is initially enhanced as compared to the monomeric double bond, due to their larger concentration near the radical site. This fact leads to an extensive primary cyclization reaction, which creates microgels, leading to heterogeneity in the polymer network[19,28,29]. Cyclization will promote higher local conversion since it does not decrease the mobility of the system as much as cross-linking. However, cyclization can lead to a reduction in the effective cross-linking density, reducing the mechanical and physical properties[19,28]. This density reduction occurs due to many of the uncured pendent double bonds becoming entrapped in the microgel regions, making further reaction inaccessible[29]. Cyclization can proceed if chain flexibility allows ring formation. On the other hand, a very stiff or long bridge between two unsaturations will prevent intramolecular cross-linking[29]. Network formation causes the reaction diffusion mechanism to be more pronounced and set at lower conversions. All these phenomena limit final conversion of double bonds to well below 100%.

In addition, network formation highly decreases the mobility of macroradicals from the very beginning of the polymerization, which is the main cause of another phenomenon: the onset of autoacceleration (gel effect) in the initial stages of the polymerization. Autoacceleration causes a rapid increase in the polymerization rate despite monomer consumption. At higher conversions, the gel effect appears to stop and the polymerization rate reaches its maximum value, then, the reaction proceeds with a decreasing rate reaching limited conversion due to vitrifiacation. For dimethacrylate monomers, the polymerization rate reaches its maximum between 20 and 40% of conversion[29]. The decrease in the polymerization rate after its maximum polymerization rate may result from several factors, such as a reduction in monomer concentration, difficulties in monomer diffusion through the solidifying medium, reduced mobility of uncured pendant double bonds and decreasing dissociation efficiency of the photo-initiator in the viscous medium[29]. At higher conversions, however, both propagation and termination processes become diffusion controlled, leading to a rapid drop in the rate of reaction, the autodeceleration. Thus, the final conversion of the polymerization is controlled by the diffusion limitations of the reacting medium and not by the amount of uncured monomer or pendant double bonds in the system[29,30].

According to Lovell *et al.*[30], the nature of the monomer molecule plays an important role in the final DC values. The viscosity of the system, when BisGMA is homo-polymerized, is so high that autoacceleration is immediate, leading to final conversion values lower than 30%. The incorporation of monomers to reduce the viscosity of the system will strongly contribute to achieve higher DC values.

The high viscosity of the BisGMA monomer (1200 Pas at 20 °C) is the consequence of strong intermolecular hydrogen bonding. This occurs because the hydroxyl groups are positioned diametrically across the rigid bisphenol core structure of the molecule, making them unable to interact and resulting in an intermolecular hydrogen bonding[31]. A significant reduction in intermolecular hydrogen bonding can be obtained with some derivatives of BisGMA, such as the BisEMA monomer, which is a non-hydroxylated homologous monomer of BisGMA[1]. This reduction in the intermolecular hydrogen bonding provides the BisEMA

monomer a greater mobility, since it presents a rigid core due to the aromatic groups. Another group of monomers used in commercial composite resins is the urethane dimethacrylates (UDMA). These monomers have molecular weights similar to that of BisGMA, but are less viscous due to a greater flexibility of the urethane linkage[1]. The viscosity of the UDMA monomer is 23.1 Pas at 20 °C[31].

BisGMA, BisEMA and UDMA compose the organic matrix of the Z250 composite resin used in this study. All these monomers present high molecular weights, but different mobilities, providing satisfactory DC values. The results found in this study are in agreement with those mentioned in the literature[13,15,18-21]. Limited final conversion is a phenomenon inherent of the polymerization process, as mentioned earlier. Although there are great differences among the used photo-activation methods, the irradiance supplied was sufficient to reach the conversion characteristics for these dimethacrylate monomer systems.

Photo-polymerization of multifunctional monomers exhibits a marked post-curing effect. After irradiation has been interrupted, the photo-induced reactions continue to proceed over a time scale of seconds, minutes or even hours. The extent of the dark reactions depends on the amount of initiating radicals generated by the irradiation step, storage temperature, as well as on the reactivity of the polymerizable function[29-30].

Table 2 shows that there was no statistical difference between two periods of storage of samples, 24 h and 20 days ($p > 0.05$). During the storage time, the specimens were maintained at room temperature and in a dark environment to avoid further photo-activation. Thus, the absence of differences between the considered storage periods may be explained by atmospheric oxygen, which reduces the extent of post-polymerization at room temperature due to the scavenging of free radicals by diffusing oxygen with the formation of peroxy and hydroperoxy radicals. These radicals are much less reactive towards double bonds, thereby reducing the efficiency of initiation and post-polymerization[29].

The results presented in Table 3 reveal that there was a significant difference between the two FTIR analysis techniques. The use of the KBr pellet technique led to higher DC values than those found when the thin resin film technique was used ($p < 0.05$). Two probable explanations for this are: (1) the negative effect of oxygen inhibition on the polymer surface which leads to the scavenging of the free radicals in this region, and (2) the exothermic nature of the polymerization reaction, what possibly caused a localized heating in the composite resin tested *via* the KBr pellet technique[20,29,32,33]. The temperature rise during the polymerization provides greater mobility to the components of reaction medium, causing higher conversion rates, as well as reducing oxygen inhibition due to a decrease in the solubility of oxygen in the polymerizing medium[29,30]. The execution of the resin film technique is simpler, however it presents DC values of a very thin, probably homogeneous, layer. Conversely, the KBr pellet technique, despite being more difficult, presents DC values of the whole composite increment, which often is non homogeneous with different DC values.

4. Conclusion

Based on the obtained results and on the method used, it can be concluded that:

- Irrespective of the storage period and specimen preparation technique, there were no significant differences among the photo-activation methods;
- No statistical difference was observed in DC values between the storage time periods used;
- The specimens analyzed by means of the KBr pellet technique presented higher DC values than those analyzed by the thin resin films.

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