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Continuous and gradual photo-activation methods: influence on degree of conversion and crosslink density of composite resins

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Abstract Thermal properties and degree of conversion (DC%) of two composite resins (microhybrid and nanocomposite) and two photo-activation methods (continuous and gradual) displayed by the light-emitting diode (LED) light-curing units (LCUs) were investigated in this study. Differential scanning calorimetry (DSC) thermal analysis technique was used to investigate the glass transition temperature (T_g) and degradation temperature. The DC% was determined by Fourier transform infrared spectroscopy (FT-IR). The results showed that the microhybrid composite resin presented the highest T_g and degradation temperature values, i.e., the best thermal stability. Gradual photo-activation methods showed higher or similar T_g and degradation temperature values when compared to continuous method. The Elipar Freelight 2^{TM} LCU showed the lowest T_g values. With respect to the DC%, the photo-activation method did not influence the final conversion of composite resins. However, Elipar Freelight 2^{TM} LCU and microhybrid resin showed the lowest DC% values. Thus, the presented results suggest that gradual method photo-activation with LED LCUs provides adequate degree of conversion without promoting changes in the polymer chain of composite resins. However, the thermal properties and final conversion of composite resins can be influenced by the kind of composite resin and LCU.

Keywords Fourier transform infrared spectroscopy · Differential scanning calorimetry · LED · Dental curing lights · Composite resins

Introduction

Owing to their excellent aesthetics, adhesion to tooth structures and improvements in the chemical and mechanical properties, composite resins are extensively used in several dentistry applications in recent decades. However, one of the main problems is the polymerization shrinkage of the matrix phase [1, 2].

Clinical failure of composite restorations is often the result of an incomplete sealing of the tooth/restoration interface. The role of polymerization shrinkage as one of the main causes of marginal integrity loss and consequent post-operative occurrences, such as hypersensitivity, microleakage, and secondary caries [3–5]. Polymerization shrinkage is related to the restorative technique employed, as well as to the composite resin composition and degree of conversion [6].

Composite resins are set via exposure to light of a certain wavelength and an intensity that initiates the generation of free radicals that propagate polymerization, causing material hardening [7–9]. This light can be emitted by light-curing units (LCUs), such as conventional quartz tungsten halogen (QTH), xenon plasma arc (PAC), argon laser and light-emitting-diodes (LEDs) [10].

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LED LCUs were introduced to the dental profession in 2001. LEDs are special semiconductors that produce electroluminescence of light in a manner completely unlike the hot filament found in QTH lights. This difference reportedly provides a longer life span, more consistent output, lower power consumption, and reduced induced. The energy from the LED is clearly defined by the semiconductor and most of the emitted light is concentrated in a narrow band around 470 nm, which is ideally suited for composite resins that use the camphorquinone photo-initiator. The second-generation LED LCUs are now similar in output and performance to high-intensity QTH curing lights and are actually superior to standard QTH curing lights. From all indications, LED curing lights are the wave of the future in visible light curing [11].

In recent years, the literature [12–16] has shown that the properties of composite resins are mainly influenced by the amount of energy delivered during irradiation. The total amount of energy per unit area, the so-called energy density, is the product of the power per unit area (power density) and the duration of irradiation. For a given energy density, different combinations of power density (PD) and curing times may be used to cure the composite materials [17].

The light from dental LCUs can be delivered in different methods: continuous, pulse-delay, or stepped irradiation. The continuous method delivers the same PD uninterruptedly throughout the entire exposure period. The pulse-delay method initiates cure by a short flash of light followed by a delay of one or more minutes before the final photo-activation is performed. In the step-cure method, a low PD is used during the first part of the photo-activation period, and a higher PD is used towards the end of the irradiation. The pulse-delay and the stepped mode of cure are the so-called soft-start methods of cure [17, 18].

The soft-start methods were introduced with the purpose of slowing down the polymerization reaction, which is inevitably accompanied by contraction of the material [19]. The different photo-activation methods and different combinations of PD and exposure duration may influence the properties of light-curing composite resins [14–16, 20–23]. It has been shown that degree of conversion, flexural strength, and flexural modulus increased with increasing energy density, and, for each energy density level, the degree of cure decreased with decreasing PD [14]. In the same way, polymerization shrinkage of composite resin increased with increasing levels of energy density, and, for each level of energy density, the shrinkage decreased with increasing PD [15].

Some authors found that soft-start photo-activation methods were able to reduce microleakage with only a discrete reduction in the degree of conversion [24]. On the other hand, others studies demonstrate that soft-start methods have resulted in either decreased degree of conversion (DC%) as compared to the one of the continuous method, or similar DC% but at the same time with polymers of lower crosslink density, reflecting on the mechanical properties [20, 21, 25, 26].

The soft-start methods of cure lead probably to the formation of relatively fewer growth centers, which may result in a more linear polymer, with decreased crosslinking. The increased concentration of crosslinks has been associated with increased physical properties and stability of polymers [25, 27].

The degree of conversion (DC%) depends on the total light energy, the irradiation times, the correct wavelength of the light source, the material composition, and others factors [13, 23, 28, 29]. All of these factors strongly influence the degree of conversion, which is the number of ethylene double carbon bonds that are converted into single bonds of the composite resin to obtain the optimal chemical–physical and clinical performance [30].

The DC% is an important parameter in determining the final physical, mechanical, and biological properties of composite resins, since it has been demonstrated that composite properties tend to improve as the degree of conversion attained during photo-polymerization is increased [31]. In addition, increased cure may result in a lower amount of uncured, potentially leachable monomer, leading to a more biocompatible restoration [22]. Moreover, uncured functional groups can act as plasticizers, reducing the mechanical properties of the composite [26].

It has been shown that the extent of crosslinking of a polymer may be assessed by measurements of the glass transition temperature (T_g). T_g is an important parameter for polymer characterization as it marks a region of dramatic changes in the physical properties of the polymer [27, 32]. The T_g value represents the temperature region at which the polymer is transformed from a glassy material into a rubberlike one. Crosslinking reduces molecular mobility, and thus gives rise to increased apparent T_g. The curing procedure may influence the regularity of the network and the crosslink density, and this may be reflected in the T_g [17, 33].

It was hypothesized that gradual photo-activation methods would exhibit a reduced crosslink density, despite the reduction of the polymerization shrinkage. In addition, lower conversion values can be obtained using this photo-activation method. Thus, the aim of this study was to investigate the effect of different photo-activation methods on degree of conversion and crosslink density of composite resins, using Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) techniques. The tested hypotheses were (1) that the photo-activation methods (continuous or gradual) affect the degree of conversion; and (2) the photo-activation methods (continuous or gradual) affect the concentration of cross-links in the composite resins.

Experimental

The information about fillers and resins matrix of the commercial dental composite resins, used in this study, are summarized in Table 1. Each represents one of two different categories of composites: microhybrid and nanocomposite.

The LCUs analyzed in this study were Elipar Freelight 2™ (3M Espe) and Bluephase® C8 (Ivoclar Vivadent). For each of the LCUs two photo-activation methods were used: continuous and gradual, pre-programmed by their manufacturers (Table 2). For Elipar Freelight 2™ (3M Espe) and Bluephase® C8 (Ivoclar Vivadent) LCUs, the continuous method delivers the same PD (996 and 860 mW cm^{-2}, respectively) uninterruptedly throughout the entire exposure period (20 s).

The gradual photo-activation method operates at low PD at the beginning and at higher PD at the end of irradiation. Thus, for Elipar Freelight 2™ (3M Espe) LCU, in the initial period of 10 s, the PD rises gradually from 0 to 996 mW cm^{-2}. For Bluephase® C8 (Ivoclar Vivadent) LCU, during in the initial period of 10 s, the PD is 150 and 860 mW cm^{-2} at the end of 10 s.

Before the curing procedures, the power output of the LCUs was measured with a calibrated power meter (Fieldmaster Power Meter, Coherent-model no. FM, set no. WX65, part no. 33-0506, USA), and the diameter of the light guide tip with a digital caliper (Mitutoyo, Tokyo, Japan). PD (mW cm^{-2}) was computed as the ratio of the output power and the area of the tip with the following formula:

$$I = P/A, \qquad (1)$$

where P is the power in milliwatts (mW), and A is the area of the light tip in squared centimeters (cm^2).

Samples preparation

For DSC and degree of conversion (DC%) measurements, the samples ($n = 3$ and $n = 5$, respectively) were made with a metallic mould (4-mm diameter and 2-mm thickness, according to ISO 4049). The mould was placed on a glass plate of 10-mm thickness. The composite resins were packed in a single increment, and the top and base surfaces were covered by a mylar strip. A glass sheet with 1-mm thickness was positioned, and a 1-kg mass was used to pack the composite resin. Then, the top surface of the samples was placed in contact with the light-curing tip.

The samples were photo-activated for 20 s (manufacturer's instructions) at room temperature, according to the group assessed (Table 3) and were stored in dry mode in light-proof containers at 37 °C for 24 h.

Differential scanning calorimetry

The DSC measurements were performed with a DSC 2910 (TA Instruments). The samples were heated at 10 °C min^{-1} from 10 to 350 °C, under nitrogen flowing at 40 mL min^{-1} to observe the T_g and degradation peak of the different groups. A mass of ~18 mg, calibrated in precision balance (Mettler AJ150), of the samples was used in an aluminum sample pan. The reference pan contained 5 mg of aluminum bulk. All the samples were previously heated until 100 °C to eliminate the thermal history of the resins, and then the DSC curves were performed.

Degree of conversion

After storing for 24 h, the samples were pulverized into a fine powder. Five milligrams of the composite powder was

Table 1 Characteristics of restorative materials used in this study (manufacturers' data)

Material	Manufacturer	Shade	Material type	Matrix	Filler size	Filler volume/%	Batch number
Filtek™ Supreme XT	3M Espe	A_2B	Nanofilled composite	Bis-GMA, Bis-EMA, UDMA, TEGDMA	Agglomerated/non-aggregated of 75-nm silica nanofiller and a loosely bound agglomerate silica nanocluster consisting of agglomerates of primary silica nanoparticles of 75-nm size fillers. The cluster size range is 0.6–1.4 μm	72.5	6ER
Filtek™ Z-250	3M Espe	A_2	Microhybrid	Bis-GMA TEGDMA UDMA and Bis-EMA 6	Zirconia/silica (medium size of 0.19 × 3.30 μm)	60	6TU

Table 2 Characteristics of light-curing units (LCUs) used in the study (manufacturers' data)

Light-curing units/serial number	Manufacturer	Continuous photo-activation method	Gradual photo-activation method
Elipar Freelight 2™/939820018167 Germany	3M Espe	Power density (PD) of 996 mW cm^{-2} for 20 s	PD 0 at 996 mW cm^{-2} for 10 s + 10 s at 996 mW cm^{-2}
Bluephase®/2124 Norway	Ivoclar Vivadent	PD 860 mW cm^{-2} for 20 s	PD at 125 mW cm^{-2} for 10 s + 10 s at 860 mW cm^{-2}

Table 3 Division of the investigated groups

Group	Composite resins	LCUs	Photo-activation methods
1 (ZEC)	Filtek™ Z-250	Elipar Freelight 2™/3M Espe	Continuous
2 (ZEG)	Filtek™ Z-250	Elipar Freelight 2™/3M Espe	Gradual
3 (XTEC)	Filtek™ Supreme XT	Elipar Freelight 2™/3M Espe	Continuous
4 (XTEG)	Filtek™ Supreme XT	Elipar Freelight 2™/3M Espe	Gradual
5 (ZBC)	Filtek™ Z-250	Bluephase®/Ivoclar Vivadent	Continuous
6 (ZBG)	Filtek™ Z-250	Bluephase®/Ivoclar Vivadent	Gradual
7 (XTBC)	Filtek™ Supreme XT	Bluephase®/Ivoclar Vivadent	Continuous
8 (XTBG)	Filtek™ Supreme XT	Bluephase®/Ivoclar Vivadent	Gradual

thoroughly mixed with 100 mg of KBr (bromide potassium) powder salt. This mixture was placed into a pelleting device and then compressed in a press with a load of 10 tons for 1 min to obtain a pellet.

The number of double carbon bonds which are converted into single bonds provides the degree of conversion (DC%) of composite resin. To measure the DC% the pellet was then placed into a holder attachment into the spectrophotometer (Nexus-470 FT-IR, Thermo Nicolet, E.U.A.). FT-IR spectra of both uncured and cured samples were analyzed using an accessory of reflectance diffuse. The measurements were recorded in absorbance operating under the following conditions: 32 scans, 4 cm^{-1} resolution, 300–4,000 cm^{-1} wavelength. The DC% was determined by subtracting the % C=C from 100%, according to the formula:

$$(\mathrm{DC\%}) = \left[1 - \left(\left(1638\ \mathrm{cm}^{-1}/1608\ \mathrm{cm}^{-1}\right)\_\mathrm{cured}/\left(1638\ \mathrm{cm}^{-1}/1608\ \mathrm{cm}^{-1}\right)\_\mathrm{uncured}\right)\right] \times 100. \quad (2)$$

The percentage of unreacted carbon–carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak at 1,638 cm^{-1}) against internal reference aromatic C=C (peak at 1,608 cm^{-1}) before and after curing of the samples.

Statistical analysis

The DC% data were analyzed by Analysis of Variance (ANOVA) at three factors and Tukey's test at the significance level of $\alpha = 0.05$.

Results and discussion

The influence of photo-activation methods provided by LED LCUs on the thermal characteristics and degree of conversion of composite resins were investigated by DSC and FT-IR methods, respectively.

Studies have shown that PD and photo-activation methods of cure influence the degree of conversion [20, 23, 24, 34–36], volume shrinkage [37, 38], elastic modulus, and T_g [17], among other properties of composite resins. Thereby, in this study, microhybrid (Filtek™ Z-250) and nanocomposite (Filtek™ Supreme XT) resins were light cured according to two photo-activation methods: continuous and gradual provided by two LED LCUs (Elipar Freelight 2™ and Bluephase® C8).

Figures 1 and 2 display the representative DSC curves obtained for the different groups investigated. The first thermal event that can be seen in the DSC curves refers to the T_g of organic phase. The temperature of T_g was about 87–130 °C, evidenced by the change in the baseline. The

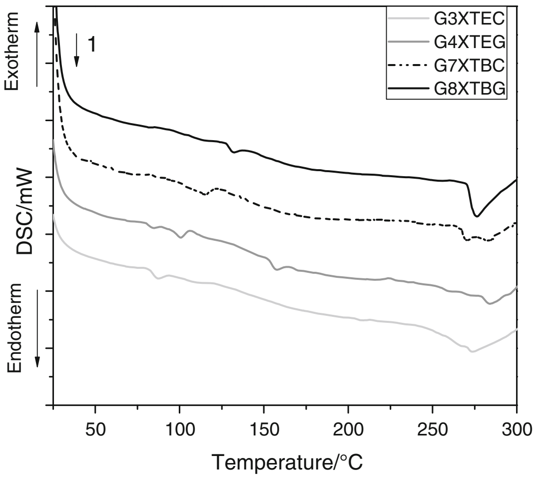

Fig. 1 DSC curves for nanocomposite groups

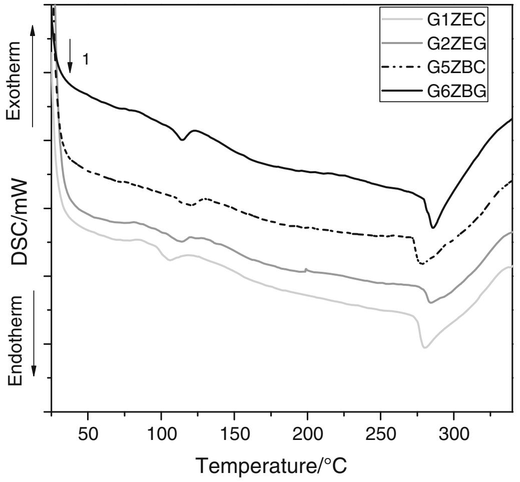

Fig. 2 DSC curves for microhybrid groups

second thermal event refers to thermal degradation peak, which occurred in the 271–289 °C range. It is known that this thermal event represents the decomposition of the composite resins [39].

The DSC can be used to determine the thermal characteristics of polymers, such as post-cure behavior, residual reactivity (amount of unreacted double bonds), and T_g [40]. T_g is an important parameter for polymer characterization as it marks a region of dramatic changes in the physical properties of the polymer. The T_g value represents the temperature region at which the polymer is transformed from a glassy material into a rubberlike one [17].

Crosslinking density of polymers reduces molecular mobility, and thus gives rise to increased apparent T_g. The curing procedure may influence the regularity of the network and the crosslink density, and this may be reflected in the T_g [17, 33]. A lower crosslink density and higher molecular mobility of the composite resins may cause a lower T_g temperature [2, 41].

It can be seen that in the groups investigated in this study the T_g values varies between 87 and 120 °C. The Filtek^{TM} Z-250 composite resin presented a higher T_g value (120 °C), while Filtek^{TM} Supreme XT presented a lower T_g value (87 °C). Despite T_g values presenting differences, these findings are in agreement with previous observations [42].

The thermal events (T_g and thermal degradation) for the groups are summarized in Table 4. From the data of Table 4, the Filtek^{TM} Z-250 presented the best thermal stability, corroborating with other studies [42]. The gradual photo-activation method showed higher T_g values or similar to the continuous method, except when Bluephase® C8 LCU was used to light-cure Filtek^{TM} Z-250 composite resin.

The Elipar Freelight 2^{TM} LCU provided lower T_g values when compared with Bluephase® C8 LCU. These data suggest that thermal properties of composite resins can be influenced by the kind of composite resin, LCU, and photo-activation methods. Likewise, thermal degradation was smaller for gradual photo-activation methods, regardless of composite resin and LCU.

Ideally, polymerization process of composite resins produces highly crosslinked network systems exhibiting good solvent resistance. However, strong structural changes may be observed during the polymerization process of multifunctional methacrylate-based composites for dental restorations, which significantly affect the final properties of the materials [43]. Thus, the study of the thermal degradation processes would provide more specific information from the internal structures of the dental composite resins.

With regard to the effect of PD on the crosslinking, it has been speculated that a slow start of the polymerization, at low PD, may result in relatively fewer growth centers, which may result in a more linear polymer structure. On the other hand, high PD led to increased crosslinked density [25, 44]. However, this observation was not found in this study.

The gradual photo-activation methods displayed by LCUs evaluated in this study consist of the continuous rise of the PD in the first 10 s (Elipar Freelight 2^{TM}) and initial PD at 125 mW cm^{-2} in the first 10 s (Bluephase® C8). As the PD maximum of the LCU is raised (996 mW cm^{-2} for Elipar Freelight 2^{TM}), probably the gradual rise in the 10 initial seconds allows that the material is most of the time radiated with PD superior to 400 mW cm^{-2}. This is a PD, considered efficient to light-cure composite resins [45]. On the order hand, LCUs based on LED have a narrow spectral range with a peak around 470 nm, which matches the optimum absorption wavelength for the activation of the camphorquinone photoinitiator. These facts can explain

Table 4 Thermal events for the groups obtained from DSC curves

Composite resins	Light-curing units	Photo-activation method	Glass transition temperature (T_g)/°C	Thermal degradation/°C
Filtek™ Supreme XT	Bluephase® C8	Continuous	115	271
		Gradual	130	286
	Elipar Freelight 2™	Continuous	87	273
		Gradual	100	283
Filtek™ Z-250	Bluephase® C8	Continuous	120	278
		Gradual	114	289
	Elipar Freelight 2™	Continuous	105	280
		Gradual	114	284

Table 5 Mean and standard deviation (SD) for degree of conversion (DC%)

Composite resins	LCUs	Photo-activation methods	Mean ± SD
Filtek™ Supreme XT	Bluephase® (Ivoclar Vivadent)	Continuous	52.23 ± 0.72 b*
Filtek™ Supreme XT	Bluephase® (Ivoclar Vivadent)	Gradual	52.30 ± 1.14 b
Filtek™ Supreme XT	Elipar Freelight 2™ (3M Espe)	Continuous	52.50 ± 1.65 b
Filtek™ Supreme XT	Elipar Freelight 2™ (3M Espe)	Gradual	51.75 ± 2.15 b
Filtek™ Z-250	Bluephase® (Ivoclar Vivadent)	Continuous	53.15 ± 1.09 b
Filtek™ Z-250	Bluephase® (Ivoclar Vivadent)	Gradual	54.46 ± 2.39 b
Filtek™ Z-250	Elipar Freelight 2™ (3M Espe)	Continuous	50.37 ± 2.03 a
Filtek™ Z-250	Elipar Freelight 2™ (3M Espe)	Gradual	48.77 ± 2.76 a

* Different letters indicate statistically significant difference at 5%

the thermal behavior of the materials with the use of gradual photo-activation methods.

As mentioned above, gradual photo-activation methods can change crosslinked density of composites. According to Dewaele et al. [17], comparisons of the continuous and the stepped photo-activation methods (evaluated in this study) are more ambiguous. This statement may be one possible explanation for the fact that gradual photo-activation methods in this study presented higher or similar T_g values compared with continuous photo-activation methods.

According to the Dewaele et al., the pulse-delay photo-activation method led to polymers of decreased T_g. Thus, the decreased T_g may be interpreted as the manifestation of a polymer structure having fewer crosslinks. In the pulse-delay curing method, after the short flash of initial light, only few growth centers remain active during the delay. In this study, pulse-delay photo-activation method was not evaluated.

The physical and mechanical properties of composite resins are directly influenced by the level of conversion attained during polymerization. The degree of conversion (DC%) is determined by the proportion of the remaining concentration of the aliphatic C=C double bonds in a cured sample relative to the total number of C=C bonds in the uncured material [46].

Techniques such as FT-IR [47, 48], RAMAN spectroscopy [42, 49], electron paramagnetic resonance (EPR) [50], nuclear magnetic resonance (NMR) [51], DSC [52] and differential thermal analysis (DTA) [53] have been used to determine the DC%. Among these, FT-IR is the most frequently used technique [46].

According to the results presented in Table 5, all the photo-activation methods showed no statistical difference among themselves ($p > 0.05$) for DC% values. These results indicate that all the tested photo-activation methods were able to cure appropriately the Filtek™ Z-250 and Filtek™ Supreme XT (both 3M Espe) composites, despite the differences (e.g., PD) among them. These results are similar to those found by other studies [2, 6, 13, 26, 34, 54, 55].

Cunha et al. [6] demonstrate that photo-activation methods using lower irradiance levels were shown to be effective in reducing the rate of stress generation without compromising the conversion of the restorative composite.

In general, dental composites reach a DC% ranging from 43 to 75%, basically depending on the composite composition, PD, and exposure time [49, 51, 53, 56, 57]. The DC% values in this study varied from 48.77% (±2.76) to 54.46% (±2.39) which also agrees with the DC% observed in other studies [6, 9, 30]. Nevertheless,

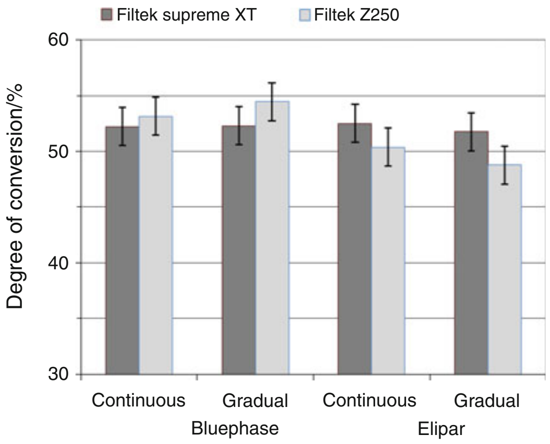

Fig. 3 Mean values of DC% depending on LCUs, photo-activation methods, and composite resins

according to Rastelli et al. [23] and Soares et al. [36] the minimum DC% for a clinically satisfactory restoration has not yet been precisely established.

The results presented reveal that there was a significant difference between the composite resins when the Elipar Freelight 2^{TM} LCU (3M Espe) was used. After 24 h, using the irradiation time recommended by the manufacturers (20 s), Filtek^{TM} Z-250 (3M Espe) resin provided the lowest values for DC%, either continuous or gradual photo-activation methods displayed by Elipar Freelight 2^{TM} (3M Espe) (50.37 and 48.77%, respectively). Degree of conversion for Filtek^{TM} Z-250 and Filtek^{TM} Supreme XT were statistically different ($p < 0.001$) when the LCU Elipar Freelight 2^{TM} (3M Espe) was used. Therefore, the results suggested that the LCU and composite resin used had a significant ($p < 0.05$) impact on the DC% (Fig. 3).

Similar results were found by Bala et al. [58]. In the samples photo-activated by Elipar Freelight^{TM} LCU, the lowest DC% value was obtained by a microhybrid composite resin Filtek^{TM} Z-250. This can be primarily explained by the difference in the composition of the resin matrix, filler size, filler volume, and filler type of the materials.

Although the organic phase of composite resins evaluated in this study are similar, there are differences in the inorganic phase (size, shape, and volume filler content). This difference in composite resins based on urethane dimethacrylates is because these materials differ in many other aspects, e.g., amount of filler, initiators, and silanation of the filler particles [58]. This statement may explain the results found in this study.

In addition, in evaluating the percentage of reacted carbon double bonds (DC%), differences in filler geometry did not seem to influence the DC% of the composites. Notwithstanding, the DC% was hindered in composites whose filler particles approached the output wavelength of the curing unit [59]. Previously, this fact was explained by the scattering effect of the penetrating light during photo-activation [60].

Finally, DSC technique allows the direct determination of the rate of polymerization reaction, assuming that the heat produced by the polymerization is proportional to the number of monomer units reacted. Rojas et al. [61] observed a good agreement between the T_g values and degree of conversion. Similar results were observed in this study.

Although the photo-activation methods had not interfered with the degree of conversion and polymer structure of composite resins in this study, more studies should be performed. In clinical practice, the gradual photo-activation methods are likely to be used to photo-activate composites in preparations, having very distinct sizes and geometries. In the literature, however, the studies that analyzed low irradiance techniques generally performed light curing with the composite in direct contact with the photo activator tip, ignoring the conjugated effect of these two light-attenuating forms on the restorative cavity [24].

Conclusions

The results obtained for this study indicate that the thermal properties (T_g and thermal degradation) of composite resins can be influenced by the kind of composite resin, LCUs, and photo-activation methods. Microhybrid composite resin presents the best thermal stability. The gradual photo-activation method provided the highest or similar T_g values compared with continuous photo-activation method, and, finally, the Elipar Freelight 2^{TM} LCU provided the lowest T_g values.

The photo-activation method did not influence on the final degree of conversion composite resins. Nevertheless, LCU and the composite resin used influenced the degree of conversion. The Elipar Freelight 2^{TM} LCU associated to microhybrid resin presented the lowest DC% mean values.

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References

1. Gatti A, Rastelli ANS, Ribeiro SJL, Messaddeq Y, Bagnato VS. Polymerization of photocurable commercial dental methacrylate-based composites. J Therm Anal Calorim. 2007;87:631–4.

2. Charton C, Falk V, Marchal P, Pla F, Colon P. Influence of T_g, viscosity and chemical structure of monomers on shrinkage stress in light-cured dimethacrylate-based dental resins. Dent Mater. 2007;23:1447–59.
3. Hilton TJ. Can modern restorative procedures and materials reliably seal cavities? In vitro investigations. Part 1. Am J Dent. 2002;15:198–210.
4. St-Georges AJ, Wilder AD Jr, Perdigão J, Swift EJ Jr. Microleakage of Class V composites using different placement and curing techniques: an in vitro study. Am J Dent. 2002;15:244–7.
5. Briso AL, Mestrener SR, Delicio G, Sundfeld RH, Bedran-Russo AK, de Alexandre RS, Ambrosano GM. Clinical assessment of postoperative sensitivity in posterior composite restorations. Oper Dent. 2007;32:421–6.
6. Cunha LG, Alonso RCB, Neves ACC, de Goes MF, Ferracane JL, Sinhoreti MAC. Degree of conversion and contraction stress development of a resin composite irradiated using halogen and led at two c-factor levels. Oper Dent. 2009;34:24–31.
7. Rueggeberg F. Contemporary issues in photocuring. Compend Contin Educ Dent Suppl. 1999;25:S4–15.
8. Deb S, Sehmi H. A comparative study of the properties of dental resin composites polymerized with plasma and halogen light. Dent Mater. 2003;19:517–22.
9. Schneider LFJ, Consani S, Ogliari F, Correr AB, Sobrinho LC, Sinhoreti MAC. Effect of time and polymerization cycle on the degree of conversion of a resin composite. Oper Dent. 2006;31:489–95.
10. Caughman WF, Rueggeberg FA. Shedding new light on composite polymerization. Oper Dent. 2002;27:636–8.
11. Leonard DL. Critical appraisal: light-emitting-diode curing lights-revisited. J Esthet Restor Dent. 2007;19:56–62.
12. Yap AUJ, Seneviratne C. Influence of light energy density on effectiveness of composite cure. Oper Dent. 2001;26:460–6.
13. Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. Dent Mater. 2002;18:463–9.
14. Peutzfeldt A, Asmussen E. Resin composite properties and energy density of light cure. J Dent Res. 2005;84:659–62.
15. Asmussen E, Peutzfeldt A. Polymerization contraction of resin composite vs energy and power density of light-cure. Eur J Oral Sci. 2005;113:417–21.
16. Calheiros FC, Kawano Y, Stansbury JW, Braga RR. Influence of radiant exposure on contraction stress, degree of conversion and mechanical properties of resin composites. Dent Mater. 2006;22:799–803.
17. Dewaele M, Asmussen E, Peutzfeldt A, Cristian Munksgaard E, Benetti AR, Finné G, Leloup G, Devaux J. Influence of curing protocol on selected properties of light-curing polymers: degree of conversion, volume contraction, elastic modulus, and glass transition temperature. Dent Mater. 2009;25:1576–84.
18. Benetti AR, Asmussen E, Munksgaard EC, Dewaele M, Peutzfeldt A, Leloup G, Devaux J. Softening and elution of monomers in ethanol. Dent Mater. 2009;25:1007–13.
19. Dewaele M, Truffier-Boutry D, Devaux J, Leloup G. Volume contraction in photocured dental resins: the shrinkage-conversion relationship revisited. Dent Mater. 2006;22:359–65.
20. Asmussen E, Peutzfeldt A. Two-step curing: influence on conversion and softening of a dental polymer. Dent Mater. 2003;19:466–70.
21. Soh MS, Yap AUJ. Influence of curing modes on crosslink density in polymer structures. J Dent. 2004;32:321–6.
22. Yap AU, Soh MS, Han TT, Siow KS. Influence of curing lights and modes on cross-link density of dental composites. Oper Dent. 2004;29:410–5.
23. Rastelli ANS, Jacomassi DP, Bagnato VS. Effect of power densities and irradiation times on the degree of conversion and temperature increase of a microhybrid dental composite resin. Laser Phys. 2008;18:1074–9.
24. Fróes-Salgado NRG, Pfeifer CSC, Francci CE, Kawano Y. Influence of photoactivation protocol and light guide distance on conversion and microleakage of composite restorations. Oper Dent. 2009;34:408–14.
25. Asmussen E, Peutzfeldt A. Influence of selected components on crosslink density in polymer structures. Eur J Oral Sci. 2001;108:282–5.
26. Asmussen E, Peutzfeldt A. Influence of pulse-delay curing on softening of polymer structures. J Dent Res. 2001;80:1570–3.
27. Tamareselvy K, Rueggeberg F. Dynamic mechanical analysis of two crosslinked copolymer systems. Dent Mater. 1994;10:290–7.
28. Rueggeberg FA, Erge JW, Mettenburg DJ. Polymerization depths of contemporary light curing units using microhardness. J Esthet Dent. 2000;12:340–9.
29. Vandewalle KS, Ferracane JL, Hilton T, Erickson RL, Sakaguchi RL. Effect of energy density on properties and marginal integrity of posterior resin composite restorations. Dent Mater. 2004;20:96–106.
30. Rastelli ANS, Jacomassi DP, Bagnato VS. Degree of conversion and temperature increase of a composite resin light cured with an argon laser and blue LED. Laser Phys. 2008;18:1570–5.
31. Lovell LG, Lu H, Elliott JE, Stansbury JW, Bowman CN. The effect of cure rate on the mechanical properties of dental resins. Dent Mater. 2001;17:504–11.
32. Anseth S, Bowman CN. Kinetic gelation model predictions of crosslinked polymer network microstructure. Chem Eng Sci. 1994;49:2207–17.
33. Groenewoud W. Characterization of polymers by thermal analysis. St Louis: Elsevier; 2001.
34. Witzel MF, Calheiros FC, Gonçalves F, Kawano Y, Braga RR. Influence of photoactivation method on conversion, mechanical properties, degradation in ethanol and contraction stress of resin-based materials. J Dent. 2005;33:773–9.
35. Obici AC, Sinhoreti MAC, Frollini E, Sobrinho LC, Goes MF, Henriques GEP. Monomer conversion at different dental composite depths using six light-curing methods. Polym Testing. 2006;25:282–8.
36. Soares LES, Liporoni PCS, Martin AA. The effect of soft-start polymerization by second generation LEDs on the degree of conversion of resin composite. Oper Dent. 2007;32:160–5.
37. Lu H, Stansbury JW, Bowman CN. Impact of curing protocol on conversion and shrinkage stress. J Dent Res. 2005;84:822–6.
38. Lopes LG, Franco EB, Pereira JC, Mondelli RFL. Effect of light-curing units and activation mode on polymerization shrinkage and shrinkage stress of composite resins. J Appl Oral Sci. 2008;16:35–42.
39. Ruyter IE, Oeysaed H. Composites for use in posterior teeth: composition and conversion. Biomed Mater Res. 1987;21:11–23.
40. Vogel BM, Mallapragada SK. Synthesis of novel biodegradable polyanhydrides containing aromatic and glycol functionality for tailoring of hydrophilicity in controlled drug delivery devices. Biomaterials. 2005;26:721–8.
41. Nomura Y, Teshima W, Tanaka N, Yoshida Y, Nahara Y, Okazaki M. Thermal analysis of dental resins cured with blue light-emitting diodes (LEDs). J Biomed Mater Res. 2002;63:209–13.
42. Bernardi MIB, Rojas SS, Andreeta MRB, Rastelli ANS, Hernandes AC, Bagnato VS. Thermal analysis and structural investigation of different dental composite resins. J Therm Anal Calorim. 2008;94:791–6.
43. Watts DC. Reaction kinetics and mechanics in photo-polymerised networks. Dent Mater. 2005;21:27–35.
44. Hofmann N, Markert T, Hugo B, Klaiber B. Effect of high intensity vs. soft-start irradiation on light-cured resin-based

composites. Part II: hardness and solubility. Am J Dent. 2004;17: 38–42.

45. Rueggeberg FA, Caughman WF, Curtis JW Jr. Effect of light intensity and exposure duration on cure of resin composite. Oper Dent. 1994;19:26–32.
46. Moraes LGP, Rocha RS, Menegazzo LM, de Araujo EB, Yukimoto K, Moraes JC. Infrared spectroscopy: a tool for determination of the degree of conversion in dental composites. J Appl Oral Sci. 2008;16:145–9.
47. Silikas N, Eliades G, Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. Dent Mater. 2000;16:292–6.
48. Stansbury JW, Dickens SH. Determination of double bond conversion in dental resins by near infrared spectroscopy. Dent Mater. 2001;17:71–9.
49. Gauthier MA, Stangel I, Ellis TH, Zhu XX. A new method for quantifying the intensity of the C=C band of dimethacrylate dental monomers in their FTIR and Raman spectra. Biomaterials. 2005;26:6440–8.
50. Sustercic D, Cevc P, Funduk N, Pintar MM. Determination of curing time in visible-light-cured composite resins of different thickness by electron paramagnetic resonance. J Mater Sci Mater Med. 1997;8:507–10.
51. Morgan DR, Kalachandra S, Shobha HK, Gunduz N, Stejskal EO. Analysis of a dimethacrylate copolymer (BisGMA and TEGDMA) network by DSC and 13C solution and solid-state NMR spectroscopy. Biomaterials. 2000;21:1897–903.
52. Antonucci JM, Toth EE. Extent of polymerization of dental resins by differential scanning calorimetry. J Dent Res. 1983;62:121–5.
53. Imazato S, McCabe JF, Tarumi H, Ehara A, Ebisu S. Degree of conversion of composites measured by DTA and FTIR. Dent Mater. 2001;17:178–83.
54. Bouschilicher MR, Rueggeberg FA. Effect of ramped light intensity on polymerization force and conversion in a photoactivated composite. J Esthet Dent. 2000;12:328–39.
55. Emami N, Söderholm KJ. How light irradiance and curing time affect monomer conversion in light-cured resin composites. Eur J Oral Sci. 2003;111:536–42.
56. Rueggeberg FA. Determination of resin cure using infrared analysis without an internal standard. Dent Mater. 1994;10: 282–6.
57. Halvorson RH, Erickson RL, Davidson CL. The effect of filler and silane content on conversion of resin-based composite. Dent Mater. 2003;19:327–33.
58. Bala O, Ölmez A, Kalayci S. Effect of LED and halogen light curing on polymerization of resin-based composites. J Oral Rehabil. 2005;32:134–40.
59. Turssi CP, Ferracane JL, Vogel K. Filler features and their effects on wear and degree of conversion of particulate dental resin composites. Biomaterials. 2005;26:4932–7.
60. Ferracane JL, Aday P, Matsumoto H, Marker VA. Relationship between shade and depth of cure for light-activated dental composite resins. Dent Mater. 1986;2:80–4.
61. Rojas SS, Frigo GJM, Bernardi MIB, Rastelli ANS, Hernandes AC, Bagnato VS. Thermal and structural properties of commercial dental resins light-cured with blue emitting diodes (LEDs). J Therm Anal Calorim. 2009. doi:10.1007/s10973-009-0521-6.