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Effects of Different Polymerization Protocols on the Degree of Conversion of Two Dual-Cured Core Buildup Composites Polymerized by Light-Emitting Diode and Halogen Light-Curing Units

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ABSTRACT: The aim of study was to investigate the effects of various curing protocols with quartz–tungsten halogen (QTH) or lightemitting diode (LED) light-curing units on the degree of conversion (% DC) of two dual-cured core buildup resin composites. Two dual-cured core buildup resin composites, Clearfil Dc Core Automix (CLF) and Grandio Core Dc (GR), were selected. Specimens were exposed to the polymerization protocols as follows: there was immediate photoactivation or photoactivation delayed by 2 or 5 min by a QTH or LED source, and one group was allowed to chemically polymerize and served as a control (n = 6). The % DC of the specimens was determined with attenuated total reflectance–Fourier transform infrared spectroscopy. The GR samples polymerized with QTH for the 5-min-delayed photoactivation had higher % DC values than those self-cured, and the Clearfil Dc Core Automix (CLF) samples with immediate or delayed curing protocols with halogen yielded higher % DC values than the samples that were chemically polymerized. The comparison of the two resin composites polymerized with LED, the % DC values of GR significantly increased after the 2-min-delayed photoactivation. In light of the results, it might be stated that CLF polymerized with QTH, could be the better option. GR provided adequate chemical polymerization; therefore, it might be useful in areas in which light curing is not possible. Clinicians should consider the polymerization characteristics of dual-cured resin composites. The use of different composites may require the modification of the application procedures recommended by the manufacturer. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40560.

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INTRODUCTION

Core buildup resin composites have been used in severely damaged teeth to restore the bulk of the coronal portion of the tooth.^{1–4} Despite the long-term success of large amalgam restorations, resin composites in combination with adequate bonding systems are currently recommended as core materials.^{2,3} The high initial strength of the resin composites expedites the clinical process because the restored teeth may be prepared for indirect restoration at the same appointment.³

Resin-based core buildup materials are available in self-curing or light-curing forms. Self-cured resin composites have the drawback of requiring a prolonged setting time that is not under the control of the clinician. On the other hand, the placement of a light-cured resin composite allows a time-saving buildup of extended foundation restorations. However, adequate polymerization cannot be ensured at deep cavities where the curing light has limited access.^{3,4} As light passes through the resin-based composite, a combination of scattering, reflection, and absorption phenomena takes place as a function of depth; this reduces the resulting irradiance energy.^{4–7} These effects result in the potential degradation of the extent of monomer conversion of the subsurface levels beyond 2 mm.⁴ The dual-cured version of resin composite buildup restoratives have recently been developed in an attempt to overcome the limitations of both self-cured and light-cured resin composite materials by the incorporation of an oxidation–reduction initiator system and photoinitiators.^{2,4,8} It has an extended working time and is capable of reaching a high degree of monomer conversion in the presence or absence of light.^{5,6} The polymerization

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of superficial areas, mainly through photoactivation results, in the rapid hardening of the resin for the initial stabilization of the restoration, whereas self-curing is designed to provide complete polymerization of the relatively deeper parts of the material that have received an insufficient light intensity.^{2,4,8,9} In general, the self-curing mechanism for dual-cured resin-based materials alone is not only slower, but it is also less effective than light activation, which was used as a supplement to the final total conversion.^{4,8,9} It has also been speculated that a delay in the light activation of dual-cured materials would enhance their properties,¹⁰ as the immediate exposure to light and the formation of crosslinked polymer chains could prevent the self-curing through the entrapment of polymerization promoters and unreacted monomers into the network, which would interfere with the self-curing mechanism.^{3,5,6,8,11}

The degree of conversion (% DC) is defined as the percentage of reacted carbon double bonds,¹² and the unreacted double bonds may either be present in free monomers or as pendant groups on the network.¹²⁻¹⁴ Unreacted monomers may leach from the polymerized material and irritate the soft tissue.¹³ Furthermore, monomers trapped in the restorations may reduce the mechanical properties.¹⁴⁻²⁰ Many studies have shown the correlation between the % DC and hardness,^{7,21} flexural strength,¹⁸ and modulus of elasticity of dental resin composites.^{15,17} Thus, a reduction in the remaining double bonds to the lowest possible level is normally considered a desirable feature of a polymerization system.²² The % DC could be assessed by direct or indirect methods, such as Fourier transform infrared (FTIR) spectroscopy,⁵ magnetic resonance imagining,⁸ optical translucency,²³ scraping,²² or hardness measurements.^{24,25} Among these methods, FTIR spectroscopy offers a direct and reliable approach for evaluating the degree of converted carbon double bonds to carbon single bonds,^{12,14,16,26} although it appears to be more expensive and time-consuming.

The success and longevity of resin composite restorations often require adequate polymerization. The curing efficiency, on the other hand, depends on the irradiance and irradiation time of the curing light and the chemical composition of the resin composite.²⁷ To improve the efficiency and time of curing, manufacturers have been developing various light sources with higher intensities.^{28,29} The efficiency of a light source can be assessed by the curing of the resin composite and subsequently by the evaluation of its mechanical, physical, and chemical properties. The curing efficiency can also be assessed by the determination of % DC.²⁸

A variety of curing light sources has now been made available to the dental profession, such as quartz–tungsten halogen (QTH), light-emitting diode (LED), laser, or plasma arc units. Among these, QTH light-curing units (LCUs) have mostly been used in clinical practices. These units have a spectrum wavelength of between 390 and 510 nm and match the peak absorption of camphorquinone (CQ), which has been used in the majority of resin composites as a photoinitiator with a maximum light absorption of 468 nm.^{16,30,31} The main radiant output from the QTH LCU is IR energy. Once absorbed by the resin composites, the energy generates heat, and this increases the molecular vibration. Therefore, filters are required to reduce the transfer of heat onto the oral structures.^{32,33} However, the degradation of the filters and the lack of maintenance of QTH LCU often decrease both the % DC values and, thus, the final quality of restoration.^{25,27–29} To overcome these problems, LED LCUs have been developed for the polymerization of dental resin composite materials. The main advantages of LED LCUs over QTH LCUs are a constant light output at 470 nm, less heat generation, no filter requirement, a much higher efficiency in converting energy to light, and a longer life expectancy.^{9,21,29,31} As some research has indicated, one possible drawback of LED LCUs could be their lower light production capacity.^{27,34} This does not appear to be a problem because LED LCUs have been shown to produce resin composite polymers with similar or superior mechanical properties to those obtained with QTH LCUs.^{16,31,35}

On the basis of the previous considerations, the aim of this *in vitro* study was to investigate the effects of various curing protocols with different polymerization times (immediately after specimen preparation or after a time delay of 2 or 5 min) and light sources (QTH or LED LCUs) on % DC of two dual-cured core buildup resin composites. The tested hypothesis indicated that the delayed light activations caused a higher % DC for both of the core resin composite materials than for those obtained with the immediate light activation. Furthermore, it was estimated that % DC of both core buildup resin composites, polymerized chemically or by immediate or delayed light activation, was dependent on the LCU and/or material.

EXPERIMENTAL

Dual-Cured Core Buildup Resin Composites

Two dual-cured core buildup resin composites [CLF and Grandio Core Dc (GR)] of the dentine shade with different filler contents and compositions were selected to determine % DC. The list of materials, including their brand names, manufacturers, and compositions (resin matrix, filler size, filler type, and filler content), is shown in Table I. Both materials were radio-opaque two-core buildup components supplied in an automix delivery system, and the working and chemical polymerization times were 3 and 6 min for CLF, respectively, and 1.5 and 5 min for GR, respectively.

LCUs

The photoactivation of the resin composites was performed with a conventional QTH LCU (Degulux, Degussa Dental, Hanau, Germany) or a blue LED LCU (Hilux 1055, Benlioglu Dental, Ankara, Turkey). The light intensity and wavelength emission of QTH were 550 mW/cm² and 400–500 nm, respectively; those of LED were 900 mW/cm² and 460–480 nm, respectively.

Specimen Preparation and Experimental Groups

The specimens were prepared in a polytetrafluoroethylene mold 4 mm in diameter and 2 mm in thickness. Each of the resin composites was prepared by the mixture of the respective base and catalyst with automix syringes according to the manufacturers' instructions. The mixture was then placed in a polytetrafluoroethylene mold positioned on a glass slide with a 1-mm thickness to obtain a smooth surface. A Mylar strip (polyethylene film) and a second glass slide (with a 1-mm thickness) were



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	CLF	GR
Manufacturer	Kuraray, Tokyo, Japan	Voco, Cuxhaven, Germany
Resin matrix	TEGDMA, Bis-GMA	TEGDMA, Bis-GMA, UDMA
Filler type	Silanated silica, silanated glass	Silica/barium glass ceramics
Average particle size (μ m)	0.04-23	0.05-5
Filler weight (%)	74	77
Filler volume (%)	52	-
Initiators	Camphorquinone and benzoylperoxide	Camphorquinone and benzoylperoxide

Table I. Manufacturers and Components of Two Dual-Cure Core Buildup Composites

^aData were provided by manufacturers.

then placed over the resin composites, and light pressure was applied to extrude the excess material. Light activation was only conducted on the top surface, during which a light-activation glass slide was used to standardize the distance from the resin to the tips of the LCUs. The upper surfaces of the specimens were exposed to light with the polymerization protocols as follows:

- Immediate photoactivation: Each of the resins was immediately light-activated in accordance with the manufacturers' recommended time points: 40 s for GR, 60 s for CLF with LED LCU, and 40 s with QTH LCU.
- Delayed photoactivation: The materials were light-activated for 2 or 5 min after the mixing of the resin was started.
- Chemical activation: No light activation was performed, and the polymerization was self-activated. This group served as a control. The details of the curing times of the resin composites are shown in Table II. Polymerization was carried out at room temperature $(23 \pm 1^{\circ}C)$. In total, 84 specimens were thus obtained (n = 6 per condition). After polymerization, the specimens were immediately covered with a lightproof adhesive tape and were then stored dry in the dark for 24 h at $37^{\circ}C$.

Measurement of % DC

The % DC of the C=C monomer of the polymerized specimens were determined by attenuated total reflectance–FTIR spectroscopy (Bruker, Vertex 80 IR, Bruker Optics, Inc., Ettlingen, Germany). The bottom surface of the specimens was put in contact

Table II. Details of the Curing Times of the Composite Resins

	Delayed time (min)	Light exposure time with QTH LCU (s)	Light exposure time with LED LCU (s)
CC	NA	0	0
CLF	2	40	60
CLF	5	40	60
GR	2	40	40
GR	5	40	40

CC, chemical curing. n = 6 per condition. NA, not applicable.

with the horizontal diamond attenuated total reflectance element in the optical bench of an FTIR spectrometer. The absorbance spectra were recorded under the following conditions: 400–4000-cm⁻¹ range, 4-cm⁻¹ resolution, and with 32 scans. The % DC was calculated with the net-peak absorbance areas of the aliphatic C=C stretching vibrations at 1638 cm⁻¹ as the analytical frequency and the aromatic C···C stretching vibrations at 1608 cm⁻¹ as the reference frequency with eq.⁽³⁶⁾:

$$\text{%DC} = \left\{ 1 - \left[\frac{A_M(\mathbf{C} \cdots \mathbf{C}) A_P(\mathbf{C} = \mathbf{C})}{A_M(\mathbf{C} = \mathbf{C}) A_P(\mathbf{C} \cdots \mathbf{C})} \right] \right\} \times 100$$

where A_M and A_P represent the net-peak absorbance height ratios of the monomer and polymer material, respectively. The IR spectra of both resin composite materials polymerized with QTH and LED are shown in Figures 1–4.

Statistical Analysis

The influence of the independent variables (the curing protocols and LCUs) on the dependent variables (% DC of the GR and CLF core buildup resin composite materials) was evaluated by a two-way analysis of variance (ANOVA) and a *post hoc* Tukey's test. A one-way ANOVA and *post hoc* Tukey's test were also performed to compare the % DC data and to compare the composite materials and LCUs for each polymerization protocol. All of the statistical analyses were performed in SPSS statistical software (SPSS, Inc., Chicago) at a 5% significance level.

RESULTS

The means (and standard deviations) for all of the experimental groups and the control group were calculated (Table III, Figure 5). A two-way ANOVA revealed that the % DC values of the GR material produced by each of the polymerization protocols displayed statistically significant differences (p = 0.019 and p < 0.05, respectively, Table III). No significant difference was found between the specimen groups prepared by different LCUs (p = 0.083 and p > 0.05, respectively, Table III). For the % DC data of CLF, statistical significant differences were recorded between the polymerization protocols (p = 0.008) and also between the LCUs (p = 0.000 and p < 0.05, respectively, Table III). Among the groups tested, the highest % DC value (80%) was attained for CLF in the case of polymerization with QTH after a 5-min delay, and the lowest value (56.83%) was also obtained for the self-cured specimens of the same material.





Figure 1. IR spectra of the CLF polymerized with QTH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 2. IR spectra of the CLF polymerized with LED. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 3. IR spectra of the GR polymerized with QTH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 4. IR spectra of the GR polymerized with LED. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Means and Standard Deviations of the % DCs (n = 6)

	Immmediate	Delayed 2 min	Delayed 5 min	Immediate	Delayed 2 min	Delayed 5 min	Chemical polymerization
GR	64.65 (9.95)	64.58A (4.57)	72.58a (3.69)	60.1 (8.17)	63.18B (5.77)	65.48 (8.02)	60.88a (4.27)
CLF	71.78b (8.65)	78.25A,c,e (3.4)	80d,f (2.21)	61.65 (9.85)	54B,e (3.79)	58f (9.18)	56.83b,c,d (5.23)

Similar capital letters in each column, and the same small letters in each row indicate statistically significance (one-way ANOVA and Tukey's post hoc test, p < 0.05). The standard deviation values are included in parentheses.

Different curing protocols appeared to have different effects on the % DC values. A one-way analysis indicated that the GR samples polymerized with QTH LCU after a 5-min delay had higher % DC values than those self-cured analogs (p < 0.05). Furthermore, immediate or delayed curing with QTH LCU yielded a higher % DC than the chemical polymerization (p < 0.05) for the CLF composite resin samples. The CLF specimens cured with QTH performed after a 2- and 5-min delays were also found to have higher % DC values than their LED analogs (p < 0.05, Table III).

When we examined the differences between the two resin composite materials, the results show that the CLF specimens cured



Figure 5. DC values (%) of the dual-cured core buildup resin in all of the polymerization protocols. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with QTH after a 2-min delay had higher % DC values than the corresponding GR specimens. On the other hand, the CLF specimens cured with LED under the same conditions yielded lower % DC values than those of the GR resin composite specimens (p < 0.05, Table III).

DISCUSSION

All of the monomers of a dental restorative resin should ideally be used up during the polymerization reaction.^{37,38} Otherwise, incomplete polymerization often leads to a lower strength and greater wear.⁷ Unincorporated monomers trapped in the restoration may also reduce the clinical serviceability of the composite through oxidation and hydrolytic degradation. Such events often manifest themselves as a discoloration of the fillings and accelerated wear.^{5,13,39} A low % DC might not only compromise mechanical properties but also reduce the biocompatibility.³ It has been well established that the final % DC of a resin depends on both the chemical structure of the dimethacrylate monomer and the polymerization conditions.^{13,31} Thus, this study evaluated the % DC values of two dual-cured core buildup resin composites having different organic matrices to determine whether the self-curing might be affected by the light energy or by the moment at which light is applied.

Although monomer conversion has been extensively measured by FTIR spectroscopy, both the techniques used for the FTIR analyses and the storage time periods after specimen preparation have not been well optimized. The storage time periods



used appear to have ranged from zero time points to several days.²⁶ In this study, FTIR measurements were performed 24 h after the completion of polymerization to obtain maximum double-bond conversion.^{5,8,15,24,38}

It has been reported that all dimethacrylate-based materials exhibit numerous residual carbon double bonds in the final product with a % DC ranging from 55 to 75% under standard irradiation conditions.⁴⁰ In general, the % DC results of all of the curing protocols used in this study remained almost within the range. Previous studies have revealed a lower % DC of dual-cured materials in the self-curing mode compared to those in the photoactivation mode.⁸ Premature photoactivation has recently been reported to interfere with the self-curing mechanism of dual-cured materials, probably by the entrapment of a large number of polymerization promoters and unreacted monomers within the rapidly crosslinked polymer network.3,5,13,39 Our results also demonstrated that the self-curing mode was not able to provide % DC values as high as those provided by the most light-activation modes. Significant differences were recorded for specimens cured with QTH. The GR specimens subjected to a 5-min delay in curing and the CLF specimens under all light-curing protocols revealed higher % DC values in comparison with those of self-curing alone (p < 0.05, Table III). These findings were in good agreement with those of previous studies.^{3–6}

Self-activation starts with the reaction between benzoyl peroxide and the tertiary amine. The mixture of these components generates free radicals; this breaks the aliphatic carbon double bonds and initiates the polymerization process. The initiator system of light activation, on the other hand, is based on CQ; this absorbs energy when the system is exposed to visible light at wavelengths between 400 and 500 nm. CQ is then combined with a tertiary amine to form a state complex that breaks down into reactive free radicals.^{41,42} Despite their independent onset,^{1,3,8} both polymerization types accomplish free-radical formation and monomer conversion and overlap during the curing process.⁴ However, Moraes et al.⁵ stated that chemical and light polymerization were interdependent and advised the use of immediate light activation in dual-cured agents. Similarly, Faria-e-Silva et al.⁶ reported that the immediate light activation of dual-cured resins yielded higher % DC values compared with chemical polymerization. Lee et al.43 described some slower curing speeds with the notion that the rapid formation of crosslinked polymer chains with light activation might lead to the entrapment of the unreacted monomers. Therefore, to prevent the premature interaction of chemical and light-curing modes, Pegaroro et al.¹⁰ recommended that the photoactivation of dual-cured resin cements could be delayed for a clinically possible time.

With the examination of the delayed and immediate photoactivation protocols performed with either QTH or LED, this study showed that the % DC values of a given resin composite did not produce statistical significant differences between the lightcuring protocols performed with the same source (p > 0.05). It was also evidenced that the delayed photoactivation did not significantly affect the % DC of the tested core buildup materials compared to those obtained with immediate light exposure. In the light of these findings, the first hypothesis was rejected. In agreement with our results, Moraes et al.⁵ reported that delayed light activation did not affect the % DC of dual-cured resin materials. Furthermore, Faria-e-Silva et al.⁶ and Pereira et al.⁸ stated that a delay time of 5 min before light activation did not interfere with the % DC of dual-cured resin agents. Because the % DC values appeared to be increased to some extent with delayed curing, we suggested that immediate photoactivation might have not hindered the migration of the activated free radicals, which were responsible for further polymerization.

It seemed that % DC of the tested materials was dependent on the type of LCU, and this supported the second hypothesis. Indeed, a meaningful difference was recorded for the CLF specimens obtained with the 2-min- and 5-min-delayed light-curing protocols. These yielded higher % DC values by QTH curing than those obtained with LED curing analogs (p < 0.05). This result was in good agreement with the studies by which Tarle et al.³⁸ and Knezević et al.,³¹ who observed that LED curing slightly lowered the % DC values. For GR core specimens, the use of QTH or LED LCUs did not lead to any significant differences in all activation modes because both of the units were effective in achieving sufficient rates of polymerization. This finding was in accordance with those of Ceballos et al.¹⁶

It has been shown that the same % DC could be produced by a fixed energy amount [Energy density $(J/cm^2) =$ Light intensity \times Irradiation time) independent of the variations within the 21-24 J/cm² energy density range.^{12,22} Because a minimum intensity of 400 mW/cm² has been suggested for routine polymerization,⁴⁴ curing lights greater than this intensity, together with the manufacturers recommended time of 40 s for GR and 40 or 60 s for CLF, was used for the comparison of our findings (Table II). The energy densities of the tested photoactivation methods varied between 22 and 36 J/cm², but the variation did not significantly affect the % DC values of the specimens. For example, in the case of CLF, LED photoactivation (36 J/cm²) produced much lower % DC values compared to QTH (22 J/ cm²). Therefore, the variations in % DC might have been caused by some other factors, such as spectral distribution of light, the polymerization reaction itself and/or the monomer system, which influenced the conversion degree of the material.26

The % DC of a resin-based material appears to depend on several factors. Stavridakis et al.⁴⁵ reported that the polymerization behavior of dual-cured resin-based composites was strongly related to the material and that it could vary as a function of the composition. For example, the organic content of composites formed by the copolymerization of dimethacrylate monomers could have a great influence on both the degree of conversion and the structure of the resulting polymer.⁴⁶ In this study, the organic matrix of CLF was based on bisphenol A glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) comonomers, and GR was based on the same comonomers plus urethane dimethacrylate (UDMA) for the partial substitution of Bis-GMA. Thus, the total organic matrix content of GR was less (23 wt %) than that of CLF (26 wt %). Although % DC of the tested composites polymerized with QTH was not found to be statistically different, except for the



2-min delay groups, the numerical lower conversion values of GR, compared to those of CLF, seemed to be related to its lesser organic matrix content and higher filler loading (77 wt %). Halvarson et al.⁴⁷ reported that the monomer conversion progressively decreased with increasing filler loading because the mobility of the resin monomers was restricted because of the existence of fillers. This may have led to decreased molecular and radical mobility and resulted in lower monomer conversion.⁴⁸

As previously stated, the % DC of UDMA was higher than expected, and this was probably due to the chain-transfer reactions.¹³ The UDMA monomer is relatively more flexible. The lower viscosities of the monomers facilitated the migration of free radicals and increased the crosslinking density.13,41,49 However, it has also been reported that the depth of curing appeared to be less in certain UDMA composites because of a greater mismatch in the refractive index between the monomer and filler.¹⁴ In addition to the resin matrix, filler particles have also been shown to possess a direct influence on the degree of curing of composite materials.^{5–7,24,30} In this study, the % DC of two composites, polymerized either with QTH or LED LCUs, yielded differences for the 2-min-delayed photoactivation, whereas QTH led to a higher % DC of the CLF, compared to that of GR, and LED caused a higher % DC in GR than in CLF. The manufacturer's working time recommendations for CLF and GR were 3 and 1.5 min, respectively. Here, we inferred that the two composites contained different concentrations of the catalyst, the amount of which could lead to different % DC values.²⁰ Unfortunately, however, no information was made available by the manufacturers indicating concentrations of the catalysts within the composites. Thus, accurate conclusions could not be drawn on the catalyst or monomer contributions to the curing efficiency.

CONCLUSIONS

In accordance with these results, it could be argued that the delayed photoactivation did not affect the % DC of both of the core buildup materials when compared to those exposed to light immediately. Although light curing with both LCUs yielded no advantages for the GR resin composites, the CLF specimens obtained by QTH LCU curing yielded higher % DC values. These findings could indicate that different dual-cured resin composites could yield different % DC values, depending on the type of the curing protocol. This conclusion could be help-ful for clinicians. It also suggests that the effects of delay time periods longer than 5 min should be included in future studies.

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