Effect of light curing and dark reaction phases on the thermomechanical properties of a Bis-GMA based dental restorative material

Roberto De Santis¹, Antonio Gloria¹, Hidehiko Sano², Eugenio Amendola¹, Davide Prisco³, Francesco Mangani⁴, Sandro Rengo³, Luigi Ambrosio¹, Luigi Nicolais⁵

¹ Institute of Composite and Biomedical Materials, National Research Council, Naples - Italy

² Department of Restorative Dentistry, Division of Oral Health Science, Hokkaido University Graduate School of Dental Medicine, Sapporo - Japan

³ School of Dentistry, University of Naples Federico II, Naples - Italy

⁴ Department of Odontostomatological Science, University of Rome Tor Vergata, Rome - Italy

⁵ Department of Materials and Production Engineering, University of Naples Federico II, Naples - Italy

ABSTRACT: *Purpose:* The effects of light curing units (LCU) and energy doses on the chemical and physical properties of a dental composite were investigated.

Methods: The effects on the chemical and physical properties of a bisphenol A diglycidylether methacrylate (Bis-GMA) based dental restorative material were evaluated through photospectrometry, differential scanning calorimetry, and mechanical measurements.

Results: The light curing conditions associated with direct and indirect restorations were replicated in vitro using optical investigation techniques. A slight attenuation resulted independently of the LCU and a strong attenuation was measured for the cement luting a thick inlay, as well as for the deepest layer of a composite filling increment. Calorimetric measurements indicated that the curing degree is very sensitive to the light energy dose rather than to the LCU. Mechanical testing showed a transient phase during which properties increased. The delay of the composite in reaching adequate properties is strongly dependent on the energy dose.

Conclusions: It is recommended that composites subject to unfavorable light curing conditions undergo a prolonged light curing process. (Journal of Applied Biomaterials & Biomechanics 2009; 7: 132-40)

Key Words: Restorative materials, Composite, Light curing, Differential scanning calorimetry, Mechanical properties

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INTRODUCTION

Polymeric composites are among the most suitable materials for manufacturing tissue replicates (1). They are very attractive materials for dental applications due to their optical properties (i.e., translucency and color) which enable successful esthetic restorations (2, 3). Composite resins are widely used for dental restorations such as the direct filling of a dental cavity (4-6), the luting of an inlay (7-9), or a dental post (10, 11). Polymeric dental composites comprise a polymeric matrix, an inorganic reinforcement (fillers), and a coupling agent (silane). The organic matrix is mainly based on Bis-GMA (bisphenol A - glycidyl methacrylate) and diluent monomers (e.g., tetraethylene glycol dimethacrylate (TEEGDMA), trieth-

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ylene glycol dimethacrylate (TEGDMA), 1,4-Butanediol dimethacrylate (BDDMA)). The polymerization process often takes place via a photoactivated reaction. Accordingly, photocurable composite resins also contain a photoinitiator system (e.g., camphorquinone/amine) and pigments (12-14).

The physical and chemical properties of the cured material are strongly dependent on the light curing process (LCP). In fact, the LCP determines the degree and extent of the polymerization. An insufficient degree of cure (DC) leads to catastrophic effects due to the reduced mechanical properties (i.e., elastic modulus and strength) (15-17) and the increased cytotoxicity (18-20). Therefore, drawbacks related to mechanical stability, marginal sealing capability, and biocompatibility are dependent on the

DC of the composite. Unfortunately, the polymerization process never reaches completion, and available theoretical approaches do not provide a reliable prediction of the network build-up as a function of the LCP (21, 22). Accordingly, investigations into the relationship between curing methods and the final properties of dental composites are predominantly based on empirical testing.

The polymer network, which rapidly forms in the LCP, continues to develop throughout the dark reaction process (DRP). Moreover, during the DRP entrapped species (monomers, free radicals, etc.), which act as plasticizers (in other words, which decrease the Young's modulus), strongly affect viscoelastic properties (12, 23). Therefore, the composite properties are a function of time and storage conditions (24-26), controlled by at least two mechanisms: the polymerization process, which continues during the DRP, and monomer leaching. From a physical point of view, the terms transient or transitory are used to describe a phenomenon or property decaying with time.

This study aimed to determine transient mechanical properties for light cured composite during the DRP. These properties are measured through bending tests on thin or thick specimens (lower or higher than 1 mm, respectively). Note that, in clinical practice, the thickness of the cement luting an inlay and the thickness of the composite increment filling a dental cavity are similar to the thickness of thin and thick specimens, respectively.

A variety of light curing units (LCUs) are available to polymerize dental composites; quartz-tungsten-halogen (QTH) lamps and light emitting diode (LED) semiconductors are the most common light sources. LCUs differ in the profile of their emitted spectrum, their power output, and their amenability to being programmed for controling the duration and level of power output. However, the light spectrum available (27-29) is approximately centered on the maximum absorption wavelength of camphorquinone (about 470 nm). To assess the LCU-dependence of properties, several light sources were employed in this study.

The degree of conversion is the parameter generally used to describe the physical properties of cured composite materials, and research on this topic is focused on the relationship between the DC and the mechanical behavior of the composite. Also, the DC depends upon geometrical properties, namely layer thickness and depth, and it is generally not uniform throughout the composite, making mechanical properties spatially dependent as well (30, 31). Moreover, the method by which the light energy is released determines the effect of shrinkage on the state of stress at the dental tissue-restoration interfaces (15, 32).

Since differential scanning calorimetry (DSC) is a very powerful tool used to investigate the curing kinetics of methacrylates (33-35), this technique has been commonly employed to monitor the forming composite through thermal measurements, therefore easily providing the DC as a function of time. In a time-temperature domain, these data are used to calibrate calorimetric models (36). DSC instruments equipped with twin optical fiber (37) measures the ability of the LCU to cure dental materials during the LCP. Also, the effects of free radicals on thermal properties can be evaluated through DSC temperature scans (25).

Summarizing, this study investigated the effects of energy doses and LCU on the chemical and physical properties of a dental composite by using photospectrometry, DSC and mechanical measurements. Light energy was varied over a broad range using several LCUs. Thermomechanical properties were observed up to one month in order to assess the dependence of the properties on the energy level and the LCU.

MATERIALS AND METHODS

Composite material

The composite material used in this study was the Enamel Plus HFO with a UD2 shade (GDF/Micerium, Genova, Italy). The amount of filler and matrix were 75% and 25% by weight, respectively. The diluent was 1,4-Butane-dioldimethacrylate (BDDMA), a monomer extensively investigated to formulate methacrylic resins (38). The matrix consisted of a Bis-GMA/BDDMA solution in the weight ratio of about 60/40, containing camphorquinone/amine as the photoinitiator system.

LCUs

Several LCUs (Tab. I) were used to cure the composite material and the energy ranged between 1.2 J/cm² and 320 J/cm². Spectra in the range of 300-900 nm were acquired using a Tristan[®] 4-Spectrometer (m·u·t GmbH, Hamburg, Germany), while power output levels were monitored with a Demetron 100 Curing Radiometer (Demetron Research Corp., Danbury, CT, USA). Figure 1 shows the emission spectrums of the study LCUs. Because the spectra of the three halogen units were similar, as were the spectra of the two light-emitting diode units, henceforth "QTH" and "LED" will be used to indicate which LCU was used in a given experiment.

The light attenuation effects on thermomechanical properties were investigated with filters made of the investigated composite material. Composite filters were polymerized with a Targis Power TP3 Upgrade (Ivoclar-Vivadent, Auckland, New Zealand) using the following curing process: 10 minutes light curing at 104 °C, 10 minutes heat curing and 5 minutes cooling. Thicknesses varied between 0.40 mm and 3.20 mm, at a pitch of 0.40 mm. The transmittance of each composite filter was assessed through spectrophotometry: measurements obtained at various distances between the light source tip and the optical sensor were compared using the composite filters



Fig. 1 - Photocuring device spectrum: a) QTH; b) LED; c) Mercury.

TABLE L - I CUS USED TO	POLYMERIZE THE	COMPOSITE	MATERIAL
INDEL 1 - LCO3 03LD TC		COMILOSHIE	

	Туре	Manufacturer	Maximum intensity [mW/cm ²]
EMS Swiss Master Light	QTH	Vallée de Joux, Geneva, Switzerland	3000
VIP	QTH	Bisco Inc Irving Park Road, Schaumburg, USA	800
Optilux	QTH	Kerr, USA	600
Elipar™ FreeLight 2	LED	3M ESPE St. Paul, USA	600-800
Luxeon LXHL-PRD5 Dental Blue V Emitter	LED	Luxeon, Calgary, Alberta, Canada	600-800
Mercury lamp Q Series	MCU	TA Instruments Waters LLC, New Castle, USA	18000

or air as medium at room temperature.

Lambert's law is used to describe light attenuation according to the equation:

$$I = I_0 e^{-\alpha x}$$
 [1]

where I is the intensity at a depth x, I_0 is the maximum intensity (i.e., the intensity at the depth x=0), and α is the attenuation coefficient.

Photocalorimetric measurements

Photocalorimetric properties were measured using the photodifferential scanning calorimeter (pDSC) Q1000 (TA Instruments Waters LLC, New Castle, DE, USA). Various photocuring conditions (differing in light source, power and exposure duration) were evaluated, operating in a nitrogen environment, and investigating isothermal photocuring at a constant temperature in the range between 25°C and 130°C. Specimens of the composite material (10±2 mg) were placed in open aluminum pans. The heat generated during the exothermal reaction was evaluated over 1 hour. In this manner, calorimetric data for each partially cured specimen were obtained throughout the course of a temperature scan (0-250°C).

Mechanical testing

Three-point bending tests at room temperature were performed with an Instron 4204 dynamometer(Instron, Narwood, MA, USA) at a crosshead speed of 1 mm/min, using two stainless steel beam supports (diameter of 2 mm) spanning 16 mm.

Two types of specimens, namely thin and thick specimens (0.40 ± 0.05 mm and 2.0 ± 0.1 mm respectively), were used to investigate the mechanical performance of a thin layer cementing an inlay or a thick layer representing an incremental filling of a direct restoration. Thin and thick specimens were polymerized into Teflon molds (length of 18 ± 1 mm). Two consecutive light curing steps were required in order to cure each specimen.

Thin samples were classified into three groups: Group A and Group B samples were polymerized through a composite filter with a thickness of 1.2 mm and 2.4 mm, respectively. The Control Group sample was polymerized at a distance of 1.2 mm between the tip of the light source and the composite material. Group B samples underwent the lowest light energy dose (1.2 J/cm²). Each specimen was conditioned at room temperature in a dark environment for 48 hours before testing. Mechanical data were analyzed following ASTM D790.

Thick specimens were used to examine the effects of



Fig. 2 - Transmittance through composite and air according to the thickness of the medium. Full and empty symbols indicate composite filter and air mediums, respectively. Round and square symbols indicate QTH and LED units, respectively.



Fig. 3 - Isothermal photocuring curves at 37°C. In the top-bottom direction each curve is obtained employing the following LCUs: a) Mercury, supplying 80 mW/cm² for 10 min; b) LED, supplying 30 mW/cm² for 40 s; c) Mercury, supplying 8 mW/cm² for 5 min; d) Mercury, supplying 8 mW/cm² for 5 min; d) Mercury, supplying 8 mW/cm² for 40 s; e) QTH supplying 5 mW/cm² for 99 s; f) QTH supplying 5 mW/cm² for 1 min.

light energy released by each LCU on mechanical properties. The range of energy spanned from a minimum of 7.5 J/cm² to a maximum of 320 J/cm²: low power (lp), middle power (mp) and high power (hp) indicated power outputs lower than 400 mW/cm², in the range of 400-600 mW/ cm², and higher than 600 mW/cm², respectively. Specimen conditioning (i.e., the duration of the DRP at room temperature in a dark environment) was investigated by detecting the Young's modulus and the maximum stress in bending at 60 seconds, 48 hours, 7 days, and 1 month.

Statistical differences among the samples (each was subjected to at least 5 measurements) were assessed using the One-way Anova at a confidence level of 99% by means of the Origin[®] 6.0 package (Microcal Software, Northampton, MA, USA).

RESULTS

A decrease in light transmission versus medium thickness was observed for both the LED and QTH curing devices (Fig. 2). This decay is due to the absorption and scattering of light through the medium, and it is steeper in the case of the composite filter. In particular, the value of transmittance through the composite with a filter thickness of 1.2 mm is close to that obtained at a distance of 15 mm in the air medium. Clinically, a decrease of about 80% in the maximum power output of the LCU is expected for the polymerization of the layer luting a typical inlay or the layer representing a deep incremental filling into a dental cavity. Figure 2 also shows that the experimental values (closed and open symbols in Fig. 2) are fairly well approximated by Lambert's exponential function (dashed curves of Fig. 2), the correlation coefficient of which is always higher than 0.99. Thus, the light intensity decreases as the thickness of the medium (i.e., filter thickness or distance in air between the light guide tip and the composite material) increases, and this decrease follows an exponential decay. The α exponent of equation [1] is lower than 1 for the composite medium, while it is higher than 1 for the air medium.

The DSC isothermal curing profiles at 37 °C are shown in Figure 3. An exothermal peak is always well evident. In the LCP, the starting steepness and the peak heat flow increase as the power output increases, thus suggesting a faster curing reaction with an increased power output. Hence, accordingly, a narrow peak is observed as the polymerization process is carried out at higher power output levels.

By comparing the curves related to mercury lamp polymerization (Fig. 3), it is evident that the lower the power output, the higher the exposure time has to be for an adequate DC at the end of the LCP. In fact, as soon as the light unit is switched off a fast decrease in heat flow is detectable for the curve obtained at 8 mW/cm² for 40 seconds of exposure.

By considering the light attenuation due to the distance of the optical fiber tip from the pan containing the composite material, the irradiation through the LED and 300 mW/cm² QTH units (Fig. 3) is estimated to be at a



Fig. 4 - DSC dynamic scans of LED cured specimens (—Control; — — Group A; --- Group B). An exothermal residual heat of reaction is clearly evident in the first dynamic scan of each sample between 45 and 140°C, thus suggesting that the polymerization process through light curing is not completed. A typical second temperature scan (— • — base line) is also shown.

power level of about 30 mW/cm² and 5 mW/cm² respectively. The isothermal curing through the LED unit used for 40 seconds clearly shows a rapid decrease in the heat flow as soon as the light unit is switched off, suggesting that, at this power level, an exposure of 40 seconds is not enough to complete the LCP. The same results are shown by the isothermal curing curves related to polymerization with the QTH unit lit for either 60 seconds or 99 seconds.

A maximum heat $Q_{max} = 60$ J/g was measured using the mercury curing unit (MCU) at 70°C with a power output of 80 mW/cm². Therefore, taking Q_{max} as the reference value (36), the DC of the composites in Figure 3 are evaluated by dividing the area underneath the peak by Q_{max} . Table II shows the heat generated and DC values obtained with the different LCUs.

Figure 4 shows the DSC dynamic scans of LED cured specimens. An exothermal residual heat of reaction is clearly evident in the first dynamic scan of each sample between 45 °C and 140 °C, thus suggesting that the polymerization process through light curing is not completed. In Figure 4, a typical second temperature scan is also shown. Table III reports the calorimetric properties of Control, Group A, and Group B specimens; the residual heat is obtained by considering the difference between the first and second DSC scans (the latter is used as base line since no further reactions are detected). It is worth noting that the exothermic



Fig. 5 - Young's modulus (a) and maximum stress (b) of thick specimens against energy levels and duration of the DRP. The bar indicates the standard deviation. Samples are classified according to the LCU, with the energy level used expressed in J/cm². Low power (lp), middle power (mp) and high power (hp) indicated power outputs lower than 400 mW/cm², in the range of 400 - 600 mW/cm², and higher than 600 mW/cm², respectively.

residual heat increases with the thickness of the filter.

Table IV shows the mechanical properties of thin specimens (thickness of 0.39 ± 0.04 mm) polymerized with the QTH and the LED curing devices, respectively. As the thickness of the filter is increased, the maximum stress decreases while the maximum strain increases. There is a statistically significant difference between the maximum stress values for the QTH-cured specimens (p<0.01), while

TABLE II - HEAT GENERATED DURING THE ISOTHERMAL CURING AND DEGREE OF CURE (DC)

	MCU 80 mW/cm ² 10 min	LED 30 mW/cm ² 40 s	QTH 5 mW/cm ² 99 s	MCU 8 mW/cm ² 60 s	QTH 5 mW/cm ² 60 s
Q [J/g]	43	39.9	31.2	25	21.3
DC [%]	72	66	52	42	35

for the LED-cured specimens the difference is only significant (p<0.01) between the Control Group and Group B samples. Also, the Young's modulus and the yielding stress decrease as the thickness of the filter is increased.

The effect of the LCU, energy level, and duration of the DRP on the mechanical properties of thick specimens are shown in Figure 5. The Young's modulus (Fig. 5a) and the maximum stress (Fig. 5b) clearly show that mechanical properties increase by increasing the energy level, at least within the first 48 hours from light curing. After one week, no difference is observed in the maximum stress, while the Young's modulus suggests a significant difference only if a wider energy range is considered. In fact, the value measured for specimens cured with a light energy of 320 J/cm² is significantly higher than the other samples (p<0.01).

Transient mechanical properties during the DRP are also evident in Figure 5. At a fixed energy level in the range between 7.5 J/cm² and 30 J/cm², mechanical properties rapidly increased within the first 2 days (p<0.01), and an increase was still measured between 2 days and 7 days at low energy levels. Interestingly, after 1 week, all the LCUs had cured the materials to achieve satisfactory properties independently of the energy dose.

DISCUSSION

The polymerization of a dental composite is achieved through an LCP and the subsequent DRP (36, 37). In fact, the extent of the polymerization at the end of the LCP is

 TABLE III - RESIDUAL HEAT AND DEGREE OF CURE (DC) GENER-ATED DURING THE FIRST DYNAMIC SCAN

	Control	Group A	Group B
Residual heat between 45 and 140 °C [J/g]	5.6	8.9	10.1
Residual heat between 145 and 165 °C [J/g]	0.5	1.1	1.6
Residual DC [%]	10	17	20

not the final DC of the composite: the material continues to polymerize during the DRP, and the DC is also dependent on the duration of the DRP. The additional polymerization which occurs during the DRP is mainly controlled by a diffusion mechanism of the trapped free radicals through a vitrified polymer matrix (12, 36); it has been suggested that the duration of the DRP can be longer than a week. As with other acrylate-based materials, the DC also determines the level of residual monomer which, by acting as a plasticizer for the forming composite, modifies the material properties (26, 36, 37).

In this scenario, it is clear that the mechanical properties of the composite are changing continuously during the DRP showing a marked transitory. It is therefore of critical importance to correlate these properties with the extent of the DRP.

Light-cured composites are used to restore teeth through both indirect and direct techniques. The former method consists of an incremental direct filling of the dental cavity, where generally each increment thickness is greater than 1 mm. The indirect method uses an inlay which is fabricated outside the oral environment and, thus, ideal laboratory conditions can be used to cure the material (7, 9). The inlay is then cemented in the dental cavity using a thin layer of luting composite; the advantage over the incremental filling technique is that polymerization shrinkage effects are strongly reduced (4-6). However, the in situ light curing of both the deepest layer of a filling increment and the film of the cement underneath an inlay are carried on at a very low power output in clinical procedures. It has been suggested that the DC of light curing composite is a function of the light energy (39) (that is the product between the power and duration of the LCP). This means that, in clinical practice, if the power level of the employed LCU is fixed, then the duration of the LCP has to be long enough to obtain an adequate DC of the composite (16, 17). Figure 2 clearly shows that a decrease in the light output higher than 80% is obtained with a filter thickness of 2 mm. Therefore, by using an LCU of 600 mW/cm², the light power supplied to the deepest layer partially filling a dental cavity can be as low as 120 mW/

TABLE IV - MECHANICAL PROPERTIES OF THIN SPECIMENS MEASURED AFTER 48 HOURS (STANDARD DEVIATIONS ARE REPORTED IN BRACKETS)

	Young's Modulus [GPa]	Maximum stress [MPa]	Maximum strain [mm/mm %]	Yielding stress [MPa]
QTH				
	7.7 (0.8)	113 (12)	1.8 (0.2)	91 (11)
	4.5 (0.7)	76 (12)	2.1 (0.4)	48 (9)
	1.5 (0.3)	41 (7)	3.5 (0.4)	21 (6)
LED				
	8.1 (1.1)	109 (14)	2.0 (0.4)	67 (10)
	5.9 (0.5)	95 (5)	2.4 (0.3)	60 (4)
	2.8 (0.4)	67 (8)	3.0 (0.5)	43 (6)

cm² and even lower (about 40 mW/cm²) for the luting material underneath an inlay with a thickness of 3.5 mm. The heat profiles at power levels lower than 80 mW/cm² recorded using the DSC (Fig. 3) and the related DC (Tab. II) clearly show that the materials are weakly converted at this power level with LCP shorter than 100 seconds. This observation is confirmed by considering the heat measured through dynamic scans (Fig. 4 and Tab. III); the residual monomer which is present in Group A and Group B materials again suggests an insufficient level of curing.

It is also observed that Young's modulus and maximum stress mean values of Control, Group A and Group B samples are statistically different (p<0.01). No difference has been detected between control samples polymerized using LED or QTH sources, while a weaker statistical difference (p<0.05) is observed for Group A and Group B.

From a clinical point of view, these thin samples, cured through a filter, can be related to the thin cementing layer underneath an inlay. The mechanical results measured after 48 hours (Tab. IV), would suggest that there is a strong dependence on the energy level employed during the LCP rather than the type of LCU. Accordingly, low energy levels lead to low mechanical properties. Moreover, calorimetric results (Fig. 4) suggest that the lower the energy level, the lower the DC, and, consequently, the greater the monomer release in the oral environment that can be expected (40).

On the other hand, the mechanical properties of thick specimens (Fig. 5) better represent the behavior of a composite incremental filling of a dental cavity. Again, properties depicted up to 48 hours are statistically higher than those obtained at 60 seconds (p<0.01); Figure 5 clearly shows dependence on the energy level employed during the LCP, rather than on the type of LCU. The increase in mechanical properties between 60 seconds and 48 hours (first and second bar rows of Figs. 5a and 5b) are consistent with the increase in DC measurements observed on several composites (41). Interestingly, after 1 week this significant difference persists only if a wider energy range is considered. It should be noted that curing modalities which use energy levels higher than 100 J/cm² are not used in clinical practice to restore a cavity through an incremental filling. Nevertheless, higher energy levels, achieved through very long LCP, are clinically recommended to cure the cementing layer underneath an inlay. A slight increase of the Young's modulus and bending strength is detected between 7 days and 1 month (Fig. 5) thus suggesting that a plateau in the mechanical properties is almost reached after 1 week. Similar results have been observed on several composites after up to 30 days of conditioning (42).

Therefore, it is clear that a transient in the properties of composite exists during which mechanical properties are enhanced. The duration of this transient is strongly energy-dose dependent. At high energy doses (i.e., 24 J/ cm²) at least two days are required before approaching satisfactory properties. As the energy level is decreased, this time delay drastically increases. Unfortunately, few studies have been implemented to determine the transient of mechanical properties during the DRP. Recently, by using indentation tests, Versluis et al (43) investigated transient mechanical properties as a function of the energy level through surface measurements. It is interesting to observe that our results suggest an extended transient, especially at low energy doses. This difference may be due to the different mechanical approach. Indentation tests (43) involve surface measurements, while testing carried out in this study refers to bulk measurements. Accordingly, the release of unreacted species (i.e., monomers), which act as plasticizers, is strongly dependent on the testing conditions.

However, both results indicate a window of energy doses inside of which transient mechanical properties are detected. As the energy level is decreased, the duration of this transient increases. At energy levels above this window the transient is very short, therefore, the material quickly approaches its best mechanical performance and properties are independent of the energy level. At energy levels below this window, the transient becomes indefinitely long.

The pictures which have been given through these results may drastically change as the conditioning environment is changed. Further research needs to be carried out in order to assess properties in wet environments at body conditions.

CONCLUSIONS

This study clearly shows that properties of light cured composite are strongly dependent on the energy level and the duration of the DRP rather than the LCU.

Within the first two days from light curing, the composite properties (i.e., stiffness and strength) increase by increasing the energy level. At a given energy level between 7.5 J/cm² and 30 J/cm², the composite properties increase by increasing the duration of the DRP. The duration of this transient strongly depends on the energy dose.

Composite cured with the same energy dose shows similar properties, independently of the LCU used. Interestingly, after 1 week from exposure to light energy higher than 7.5 J/cm², similar, adequate properties are observed. Therefore, it is concluded that properties of light-cured composite are strongly dependent on both the energy dose and the duration of the DRP rather than on the LCU.

From a clinical point of view, a layer underneath a thick inlay or the deepest layer of a composite incremental filling are subject to a significant decrease in light power. Under these conditions, the delay that the composite shows before approaching satisfactory properties can be long enough to allow mechanical damage caused by mastication or the inflammatory process of the pulp-dentin organ due to the release of monomer from a weakly converted material. Therefore, a prolonged LCP duration, that is, the exposure time of the material to light, is recommended in order to promote satisfactory properties.

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Address for correspondence: Antonio Gloria Institute of Composite and Biomedical Materials National Research Council Piazzale Tecchio, 80 80125 Naples - Italy angloria@unina.it

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