

# The effect of the light curing source and of the photoinitiation system on the light cured adhesive systems

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**Purpose:** It is assumed, that, by following the manufacturers' instructions regarding the polymerization methodology and using two curing lamps with different technologies, the result will be the same in terms of degree of conversion of the monomers.

**Materials and Methods:** Two commercial adhesives and one experimental adhesive were taken into study. The samples were polymerized with two different light source and analyzed by FTIR techniques.

**Results:** The results of the statistical tests showed there is a significant difference between the two sources of polymerization only in the case of the adhesive system which does not use camphorquinone as a photoinitiator.

**Conclusion:** The permanent evolution of light curing materials and of their photoinitiation systems may lead to a gap between the polymerization capacity of the common light sources and the real needs of the materials.

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## 1. Introduction

Light curing units are widely used in dental offices. Materials and equipment have evolved. But sometimes the benefits may turn into disadvantages. A high specialization may prevent adaptation to the continuously changing environment. The field of the light curing composite materials together with the associated equipments is one of the most dynamic in the contemporary dental practice.

The halogen lamps with all their disadvantages, the gliding of the emission spectrum towards red, the reduced lifetime, the defective filters guides still remain of importance for the dentist.

In theory, the LED lights are considered highly superior. The heat emitted by the diodes and transmitted to the material is low, the light emission is constant in terms of wave length and intensity of radiation, the light spectrum is narrow, around 468 nm, the depth of cure is higher compared to the halogen lamps, the current consumption is reduced by 95 %, the life is increased, they are more ergonomic.[7]

The polymerization reaction depends on several factors:

- The temperature of reaction [10]
- The structure and functionality of the monomers [1]
- The quality of the solvents [3]

- The presence of oxygene, contact which can not be avoided during the clinical application [8]
- Humidity [12]
- Viscosity [2]
- The polymerization protocol related to the intensity of light [5]
- The photoinitiator type [12]

It is assumed, that, by following the manufacturers' instructions regarding the polymerization methodology and using two curing lamps with different technologies, the result will be the same in terms of degree of conversion of the monomers.

The experiment uses besides commercial adhesives, one experimental adhesive.

The null hypothesis of the experiment implies that there will not be any differences between the two sources of polymerization.

## 2. Materials and methods

Two commercial adhesives and one experimental adhesive were taken into study: a commercial adhesive of the type one step total etch Single Bond 2 (3M ESPE), a commercial adhesive of the type one step self-etch Adper Prompt L-Pop (3M ESPE) and an experimental adhesive of the type two step self-etch (Table 1).

Table 1. The composition of the adhesive systems and photoinitiation systems; BIS-GMA – bisfenol A diglycidyl ether dimetacrylate; HEMA – 2-hydroxyethyl metacrylate; TEG-DMA - triethyleneglycol dimethacrylate; DMAEMA - dimethylaminoethyl methacrylate.

Adhesive	Composition	Photoinitiator
Single Bond 2	ETHYL ALCOHOL SILANE TREATED SILICA (NANOFILLER) BIS-GMA, HEMA, GLYCEROL 1,3-DIMETHACRYLATE COPOLYMER OF ACRYLIC AND ITACONIC ACIDS WATER DIURETHANE DIMETHACRYLATE	NA but not camphorquinone
Adper Prompt L-Pop	WATER HEMA DI-HEMA PHOSPHATE BIS-GMA	ETHYL 4-DIMETHYL AMINOBENZOATE DL-CAMPHORQUINONE
2 step experimental adhesive	HEMA, URETHANE MONOMER WITH PHOSPHORUS, ETHYL ALCOHOL, WATER, BIS-GMA, TEG-DMA	camphorquinone with DMAEMA, difenil iodonium chloride

Polymerized adhesive samples (n=5) were prepared with a diameter of 5 mm and a thickness of 1mm. The polymerization was performed through a transparent film of plastic material from a distance of 0,5 mm with Elipar 2500 (3M ESPE) and Elipar Freelight 2 (3M ESPE) respecting the polymerization protocol presented in Table 2. Polymerization time was chosen on the basis of total energy density .

Table 2. Light curing lamps used in the experiment and their main characteristics.

Polymerization source	with halogen Elipar 2500 (3M ESPE) light	Elipar Freelight 2 LED, (3M ESPE)
Energy density	500mW/cm <sup>2</sup> (estimation)	1000mW/cm <sup>2</sup>
Polymerization time	20 sec	10 sec.
Ø guide	Ø 8 mm	Ø 8 mm

The samples were studied by the absorption spectrometry technique in the IR spectral band, using FT-IR JASCO 610 immediately after polymerization.

For the quantitative determination of the unreactive metacrylate groups there is used the absorption band from 1637 cm<sup>-1</sup> due to the valence vibrations of the double bonds C=C from the metacrylate groups. As an internal

standard, there is used the C-C absorption band from 1608 cm<sup>-1</sup>, due to the valence vibrations of the aromatic nuclei of the Bis-GMA molecule. The report of the absorbent intensity C=C/C-C is measured before and after the polymerization.

The double residual bonds are calculated according to following formula [6]:

$$\%(C = C) = \left[ \frac{\left[ \frac{Abs_{\nu_{C=C}}}{Abs_{\nu_{ref}}} \right]_{\text{Polimer}}}{\left[ \frac{Abs_{\nu_{C=C}}}{Abs_{\nu_{ref}}} \right]_{\text{Monomer}}} \right] \times 100$$

The polymerization source was determined as an independent variable as it is the parameter which was modified during the experiment.

The mathematic representation of the null hypothesis using symbols is as follows:

$$\%(C = C)(Halo) \cong \%(C = C)(LED)$$

Entering the calculation formula of the remaining double residual bonds in this relationship following relationship is obtained:

$$\left[ \frac{\left[ \frac{Abs_{\nu_{C=C}}}{Abs_{\nu_{ref}}} \right]_{\text{Polimer (Halo)}}}{\left[ \frac{Abs_{\nu_{C=C}}}{Abs_{\nu_{ref}}} \right]_{\text{Monomer}}} \right] \times 100 \cong \left[ \frac{\left[ \frac{Abs_{\nu_{C=C}}}{Abs_{\nu_{ref}}} \right]_{\text{Polimer (LED)}}}{\left[ \frac{Abs_{\nu_{C=C}}}{Abs_{\nu_{ref}}} \right]_{\text{Monomer}}} \right] \times 100$$

The absorbance report for the non-polymerized adhesive solutions is the same for both parts of the formula and can be considered a constant.

By simplifying the formula one obtains the report of absorbencies for the studied samples as a dependent variable in the study.

$$\left[ \frac{Abs v_c = c}{Abs v_{ref}} \right] \text{Polimer (Halo)} \cong \left[ \frac{Abs v_c = c}{Abs v_{ref}} \right] \text{Polimer (LED)}$$

### 3. Results

The data resulting from statistical analysis, from the report of absorbencies for the three adhesives and the two polymerization sources is summarized in Table 3.

Table 3. Statistical analysis of the values resulting from the reports of absorbencies.

Adhesive	Halogen		LED	
	Mean	StDev	Mean	StDev
SB2	0,9834	0,0168	1,0331	0,0125
AP	1,3404	0,0269	1,3797	0,0318
SA2	1,1620	0,1730	1,1850	0,2240

The values were tested for normal distribution with the Anderson-Darling and the Kolmogorov-Smirnov tests. Both tests confirmed the normal distribution of the values and, as a result, we used the t-test, (two sample, two tail) for the evaluation of the independent variable influence on the values obtained for the dependent variable.

In Table 4 are presented the calculated values in the t test and the statistical significance of the results ( $p < 0,05$ ).

Table 4. Values from test t: a – significant statistic difference; b – insignificant statistic difference.

Adhesive	T(two tail)	P	Statistic significance
SB2	-5,30	0,001	a
AP	-2,11	0,072	b
SA2	-0,18	0,865	b

The results of the statistical tests showed there is a significant difference between the two sources of polymerization only in the case of the adhesive system Single Bond 2 (3M ESPE) which does not use camphorquinone as a photoinitiator. The halogen curing unit performed better than the LED lamp.

For Adper Prompt L-Pop (3M ESPE) and the experimental SA2 adhesives which use camphorquinone

as a photoinitiator the resulted differences were insignificant.

### 4. Discussion

The degree of conversion reached after the polymerization of the monomers substantially affects the properties of the adhesives used in stomatology. The monomers that make up the organic phase of the adhesives are mostly dimethacrylated. These dimethacrylates copolymerize and form an organic matrix with a three dimensional reticulate structure. This structure contains residual unsaturation, in the form of methacrylate pendant groups. Depending on the structure of the monomers, these unreactive methacrylate groups can be longer or shorter turning the adhesive material less resistant to the degradation reactions.

The emission spectrum of the halogen light is very wide. In order for light to be useful, the emitted light is filtered so that only the photons from the spectral band of 400-500 nm are transmitted to the photopolymerizable material. This spectral band was chosen because it meets the absorption band of most frequently used photoinitiator systems.

The emission spectrum of the LED lights is very narrow and may not meet the maximum of absorption of the photoinitiators; this may lead to a low internal conversion rate and to deficient physicochemical properties. [7]

The study of the photopolymerization source effect on the photopolymerizable materials requires the determination of the polymerization source as an independent variable. The statistic study is significantly clinically if the factors which build the independent variable are controlled within the experiment or are clinically relevant.

The efficiency of the light curing lamps depends on the emission spectrum of the lamp, on the polymerization light power density and on the necessary time to release the right energy for the photopolymerization reaction.

Examining these parameters and their clinical application one will find out, that for turning the power density and the polymerization time into constants there would be necessary to use two light curing lamps with halogen light simultaneously, which deliver together a power density of 1000mW/cm<sup>2</sup>, similar to the LED light. Clinically, such an approach is unrealistic, reason for which we controlled these parameters by means of total energy density, obtaining thus a second variable parameter, time.

The independent variable depends on the spectrum of light polarization and on the time required for the supply of polymerization energy, respectively on the factors which are taken into account when choosing the polymerization source in the praxis.

The degree of conversion from monomer to polymer may be influenced by the system of photoinitiation used (12).

In this experiment the activators used have been:

- DL-CAMPHORQUINONE ETHYL 4-DIMETHYL AMINOBENZOATE which can be found in the Adper Prompt L-Pop adhesive,

- camphorquinone with DMAEMA and difenil-iodonium-chloride which can be found in the experimental two step self etching adhesive

- the chemical formula of the photoinitiator is not specified in the composition of the Single Bond 2 commercial adhesive, but this is not camphorquinone, the different results of this product being thus explained.

The information regarding the polymerization LED lamp provided by the manufacturer indicate the centering of the emission spectrum of the light on the maximum absorption band of camphorquinone, around the value of 470 nm. As a consequence of this, the polymerization lamp will not be able to be applied to all photopolymerizable materials, thing which is mentioned by the producer in the data sheet.

The narrow emission spectrum of the LED lamp also had an impact on the adhesives used in this study, triggering a significant difference in the adhesive that does not use camphorquinone as a photoinitiator.

Recent studies suggest the existence of a relationship between the hydrophobic / hydrophilic photopolymerization activation system and the degree of conversion of the monomers to polymers. In the presence of water occurs a nano-phase separation between HEMA and Bis-GMA, which affects the formation mechanism of the copolymers. If one would add the hydrophobic / hydrophilic character of the activator, there would occur areas with different degrees of polymerization.

Such an irregular structure of the polymer would have a negative influence on the physical properties of the adhesive. [4, 9, 11, 13].

## 5. Conclusions

The permanent evolution of light curing materials and of their photoinitiation systems may lead to a gap between the polymerization capacity of the common light sources and the real needs of the materials.

The LED lights are more efficient than the halogen lights in terms of ergonomics and energetic efficiency but their rather narrow emission spectrum may act negatively on the degree of conversion of the monomers of the adhesive system.

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