

Effect of diphenyliodonium hexafluorophosphate in the yellowing and properties of experimental resin cements

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Received: February 26, 2019

Accepted: September 16, 2019

Aim: The yellowing effect is undesirable and can occur in the dental restoration margins when light-cured resin cements containing camphorquinone as photoinitiator is used. This study aimed to evaluate the effect of diphenyliodonium hexafluorophosphate (DPI) in photoinitiator systems that contained different concentrations of camphorquinone (CQ) and dimethylamino ethyl benzoate (EDAB) on resin cements. **Methods:** A base (1:1) of bisphenol A diglycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) was obtained, and 60wt% of glass fillers was added. Eight formulations were obtained: RC1 (0.5mol% CQ / 1mol% EDAB), RC2 (0.5mol% CQ / 2mol% EDAB), RC3 (1mol% CQ / 1mol% EDAB), RC4 (1mol% CQ / 2mol% EDAB), and RC5 to RC8, which contained the same bases plus 0.5mol% DPI. Experimental resin cements were evaluated by the degree of conversion (DC), L*a*b* color analysis, water sorption (WS) and solubility (S), flexural strength, and Elastic Modulus. The data were analyzed by three-way ANOVA, Tukey's and Mann-Whitney tests ($\alpha = 0.05$). **Results:** The combination of DPI and 0.5mol% CQ increased DC in RC6 and L* in RC5 without increasing the WS and a* b* values. CQ at 1mol% showed higher values of b* and lower values of a*, except for RC3. Groups with 2mol% EDAB showed higher DC. **Conclusion:** The addition of DPI reduces CQ, generating a decreased yellowing effect, while maintaining adequate properties in the resin cements, especially with 2 mol% EDAB.

Keywords: Resin cements. Physical phenomena. Photoinitiators, dental. Polymers.



Introduction

Resin cements are widely used in luting procedures, such as laminate veneers, crowns, and posts. However, the choice of a light-cured or dual-cured fixation agent depends on the intended use¹. The thickness of larger indirect restorations and the depth in root post fixations are factors that usually suggest the choice of dual-cured resin cements because of their distance from the light source. In these cases, dual-cured resin cements may perform better when the light power is reduced². Despite the advantage of chemical phase polymerization, the amount of tertiary amines in these materials is a potential factor for yellowing, because of the possibility of oxidation of these molecules. Light-cured resin cements are more stable with a reduced tertiary amine concentration, which also provides a longer working time, leading to easier removal of excess resin during procedures³. Improving the photoinitiator system can be an alternative to these materials that have limited indications.

Camphorquinone (CQ) is the most common photoinitiator that is used for composites^{4,5}. Recently, total or partial replacement of this component was described as a possibility for providing better properties, such as a higher degree of conversion (DC). CQ is an intense yellow powder with a conjugated diketone chromophore. Because of this coloration, greater amounts of CQ in a resin cement may impact the optical properties of restorations over time, marking the margins of restoration in esthetic areas and altering the color aspect of thin laminates because of the resin cement color change⁶. Because of this characteristic, reducing this component in initiator systems may decrease these undesirable effects on the composite color^{6,7}. Polymerization is generally initiated using CQ/amine systems, because, although reactions can occur using only the CQ, they are more effective with a co-initiator as a reducing agent. Dimethylamino ethyl benzoate (EDAB) is described as a tertiary aromatic amine in two-component photoinitiator systems that interacts with CQ to form exciplexes that lead to efficient free radical formation⁸.

An iodonium salt, diphenyliodonium hexafluorophosphate (DPI), has been investigated to improve polymerization in metacrylate-based resins and cements as the third molecule in a three-component photoinitiator system⁹. During the interaction with an excited photosensitive initiator, such as the CQ, DPI can be decomposed into diphenyliodine. Diphenyliodine generates phenyliodine and phenyl free radicals, which initiate polymerization in metacrylates. Another mechanism can occur when amino radicals produced from CQ/amine reduce DPI, also generating new free radicals. Phenyl radicals generated in these ways can still react with residual amines and form new free amine radicals, which may be associated with better polymerization¹⁰. The C-I bond in iodonium salts has a low energy, which can explain its decomposition in these ways during the reactions¹¹.

However, the adequate concentration of each component of photoinitiator system that provides the least amount of yellowing of resin cements using CQ as photoinitiator remains unclear. Thus, it is important to investigate ternary systems using iodonium salt and the influence of each component and concentration on chemical and

physical properties of resin cements; previous studies did not change the concentrations of CQ and EDAB associated with DPI in resin cements, to achieve the best combination⁹. Adding DPI may allow CQ reduction, which may improve color and provide better esthetic results. The objective of the present study was to evaluate the influence of adding DPI to different concentrations of CQ/EDAB in ternary systems on the DC, color analysis (Y), water sorption (WS), solubility (S), flexural strength (FS), and elastic modulus (E). The hypotheses tested were as follows: (1) As the concentration of CQ/EDAB combined with DPI increases, the cement's properties will also improve; (2) DPI does not affect color; and (3) the lower the CQ concentration, the lower the yellowing effect.

MATERIALS AND METHODS

Preparation of the model cements

Experimental resin cements (RC) were prepared at a 1:1 mass ratio of bisphenol A diglycidyl methacrylate (BisGMA, Esstech Inc., Essington, PA, USA) and triethyleneglycol dimethacrylate (TEGDMA, Esstech Inc., Essington, PA, USA). Butylated hydroxytoluene (BHT, Esstech Inc., Essington, PA, USA) was added as an inhibitor at 0.1 mol%. Four resin cements were tested using binary systems with 0.5 mol% or 1 mol% camphorquinone (CQ, Sigma–Aldrich, St. Louis, MO, USA) and 1 mol% or 2 mol% EDAB (Sigma–Aldrich), totaling eight formulations. Diphenyliodonium hexafluorophosphate (DPI, Sigma–Aldrich, Milwaukee, WI, USA) at 0.5 mol% was added in the other four resin cements, forming ternary systems according to the following proportion in mol%:

RC1: CQ + EDAB (0.5/1)

RC2: CQ + EDAB (0.5/2)

RC3: CQ + EDAB (1/1)

RC4: CQ + EDAB (1/2)

RC5: CQ + EDAB + DPI (0.5/1/0.5)

RC6: CQ + EDAB + DPI (0.5/2/0.5)

RC7: CQ + EDAB + DPI (1/1/ 0.5)

RC8: CQ + EDAB + DPI (1/2/0.5)

The resins were blended and homogenized for 1 h at room temperature with a magnetic stirrer. Each formulation was loaded with 60 wt% of 0.7 μm average size silanated barium borosilicate glass fillers (Esstech Inc., Essington, PA, USA). All chemicals were used without further purification.

Degree of conversion

For the DC assessment, five specimens from each group were prepared directly on the horizontal face of the attenuated total reflectance (ATR) cell using a diamond crystal (Pike Technologies, Madison, WI, USA) in Fourier Transform Infrared Spec-

troscopy (FTIR, Spectrum 100 Optica, PerkinElmer, Billerica, MA, USA). A silicon bar mold (7 mm long, 2 mm wide and 1 mm high) was filled with material directly on the crystal, and a Mylar strip was placed over the mold for polymerization with a light-emitting diode (LED, Bluephase G2, Ivoclar-Vivadent, Schaan, Liechtenstein) at an irradiance of 1.200 mW/cm² for 20 s. The assay was performed at the bottom surface immediately after the light-curing protocol. Before polymerization, the monomers' baseline was recorded with a wave-number range of 1.665–1.580 cm⁻¹, resolution of 4 cm⁻¹, and Happ-Genzel apodization in absorbance mode (12). The DC was calculated according to a baseline technique based on band ratios of 1.638 cm⁻¹ (aliphatic carbon-to-carbon double bond) and 1.608 cm⁻¹ (aromatic component group) as an internal standard between the polymerized and unpolymerized samples, based on the following expression: $DC=100 \times [1 - (\text{polymerized cement}/\text{unpolymerized cement})]$.

Color analysis

Silicon molds (5 mm in diameter and 1 mm thick) were filled with resin cements and irradiated for 20 s using light-emitting diodes (LED, Bluephase G2, Ivoclar-Vivadent) through a Mylar strip. Ten specimens of each group were stored dry in a dark container for 24 h at room temperature (25±1°C). The color reading was performed using a reflectance spectrophotometer (Konica Minolta CM-700d, Shanghai, China) with a Teflon device as a sample holder. A light cabin (GTI mini matcher MM1e; GTI Graphic Technology, Newburgh, NY, USA) was used during measurements to standardize the ambient light. CIE Lab system was used to quantify the values considering the coordinates L* (Luminosity, from 0=black to 100=white), a* (from negative values=green to positive values=red), and b* (from negative values=blue to positive values=yellow).

Water sorption and solubility

Five specimens of each group were prepared in a silicon mold (7 mm long, 2 mm wide, and 1 mm high). The reduced specimen dimensions were adapted to enable a single-step light-curing of resin cements for 20 s with light-emitting diodes (LED, Bluephase G2, Ivoclar-Vivadent). The specimens were individually stored in microtubes at 37°C, in a desiccator with silica gel. They were weighed daily in an analytical balance (Discovery DV215CD, Ohaus Corporation, Pine Brook, NJ, USA) with an accuracy of 0.01 mg. This procedure was performed three consecutive times until the loss of mass in each specimen was no higher than 0.1 mg each. These values were recorded as m1. The length, width, and height of the specimens were measured using a digital caliper (Mitutuyo, Tokyo, Japan) with 0.01 mm accuracy for calculation of the volume (V) of each bar, in mm³. The specimens were then individually immersed in 3 ml of distilled water for 7 days. After immersion, the excess water was removed using absorbent papers and the specimens were gently dried with air for 10 s and weighed again to record m2 values. For recording of m3 values, specimens were stored again in a desiccator containing silica gel and weighed as described in the process for m1. The values of WS and S were calculated according to the formula: $WS=(m2-m3)/V$ and $S=(m1-m3)/V$.

Flexural strength and elastic modulus

For three-point bending measurements ($n=10$), specimens were made in a similar way to that used for the WS and S, in bar-shaped specimens (7 mm long, 2 mm wide and 1 mm high). The specimens were irradiated for 20 s by light-emitting diodes (LED, Bluephase G2, Ivoclar-Vivadent). After storage for 24 h, their dimensions were measured using an electronic digital caliper (Mitutuyo, Tokyo, Japan), and the specimens were tested on a universal testing machine (Instron 4411, Canton, MA, USA) with a span width of 5 mm at a crosshead speed of 0.5 mm/min with 50N. FS and E were monitored by Blue Hill 2 software (Instron). FS (MPa) was calculated according to the formula: $FS=3F/2bh^2$ where: F is the maximum load in Newtons that is exerted on the specimen, l is the distance between the supports; b is the width of the specimen immediately before testing (mm); and h is the height of the specimen immediately before testing (mm).

The values of E were obtained from the linear portion of load-displacement traces generated by the software, according to the formula: $E=(\Delta F/\Delta y) \times (3l/4bh^3)$, where $\Delta F/\Delta y$ is the force variation (ΔF) divided by unit change in deflection at the center of the specimen (Δy), l is the distance between the supports; b is the width of the specimen immediately prior to testing (mm); and h is the height of specimen immediately prior to testing (mm).

Statistical analysis

The normality and variance homogeneity of the data were analyzed. The results of DC, WS/S, FS/E, and coordinates a^*b^* of the color analysis were analyzed using a three-way ANOVA and Tukey's post-hoc test ($\alpha=0.05$). The results of L^* were analyzed using the non-parametric Mann-Whitney U test ($\alpha=0.05$).

RESULTS

Degree of conversion

Table 1 shows that when EDAB was used at 1 mol%, there was no difference between the groups regardless of the concentration of CQ and the presence of DPI. Adding DPI increased the DC for 0.5 mol% CQ and 2 mol% EDAB cement. However, without salt, the cement containing 1 mol% CQ and 2 mol% EDAB had higher results. For amines, the 2 mol% EDAB cements promoted better results than the 1 mol% cements.

Table 1. Means (standard deviations) for DC (%)

| DPI (mol%) | CQ (mol%) | EDAB (1 mol%) | EDAB (2 mol%) |
|------------|-----------|-----------------|------------------|
| 0 | 0.5 | 51.17 (0.22) Ab | 53.09 (0.37) Ba# |
| | 1 | 50.68 (0.33) Ab | 56.05 (0.61) Aa# |
| 0.5 | 0.5 | 51.51 (0.44) Ab | 55.54 (0.78) Aa* |
| | 1 | 51.52 (0.80) Ab | 54.12 (0.44) Ba* |

Values followed by the different upper case letter in the same column or by different lower case letter in the same row are statistically different ($p < 0.05$). * and # represents statistical difference for DPI.

Color analysis

Color analysis considered the results of coordinates L*a*b* separately. Table 2 shows that adding DPI increased the L* when combined with 0.5 mol% CQ and 1 mol% EDAB. For coordinate a*, Table 3 shows the influence of DPI when combined with 1 mol% CQ and 1 mol% EDAB, which caused decreasing values.

Table 2. Median (minimum - maximum) of coordinate L*

| DPI (mol%) | CQ (mol%) | EDAB (1 mol%) | EDAB (2 mol%) |
|------------|-----------|---------------------------|--------------------------|
| 0 | 0.5 | 82.27 (79.34 - 83.60) Aa* | 81.94 (80.53 - 83.26) Aa |
| | 1 | 82.85 (81.97 - 83.24) Aa | 82.27 (81.65 - 82.86) Ab |
| 0.5 | 0.5 | 83.11 (82.40 - 83.53) Aa# | 82.45 (80.96 - 83.27) Ab |
| | 1 | 82.75 (81.68 - 83.00) Aa | 82.70 (81.56 - 83.28) Aa |

Values followed by the different upper case letter in the same column or by different lower case letter in the same row are statistically different ($p < 0.05$). * and # represents statistical difference for DPI.

Table 3. Means (standard deviation) of coordinate a*

| DPI (mol%) | CQ (mol%) | EDAB (1 mol%) | EDAB (2 mol%) |
|------------|-----------|------------------|-----------------|
| 0 | 0.5 | -1.55 (0.15) Ab | -1.89 (0.23) Ba |
| | 1 | -1.69 (0.45) Ab* | -2.52 (0.36) Aa |
| 0.5 | 0.5 | -1.72 (0.11) Ba | -1.84 (0.21) Ba |
| | 1 | -2.29 (0.20) Aa# | -2.43 (0.26) Aa |

Values followed by the different upper case letter in the same column or by different lower case letter in the same row are statistically different ($p < 0.05$). * and # represents statistical difference for DPI.

Table 4 shows that DPI also affected b* values when added into cements containing 1 mol% CQ and 1 mol% EDAB, which caused increasing results. The EDAB concentration of 2 mol% showed higher values than 1 mol% EDAB when combined with 1 mol% CQ or 0.5 mol% CQ with 0.5 mol% DPI. However, in all experimental resin cements tested, 1 mol% CQ produced a higher yellowing effect than 0.5 mol%.

Table 4. Means (standard deviation) of coordinate b*

| DPI (mol%) | CQ (mol%) | EDAB (1 mol%) | EDAB (2 mol%) |
|------------|-----------|------------------|-----------------|
| 0 | 0.5 | 7.75 (0.68) Ba | 8.24 (0.50) Ba |
| | 1 | 9.49 (1.74) Ab* | 11.96 (1.00) Aa |
| 0.5 | 0.5 | 7.33 (0.52) Bb | 8.91 (0.99) Ba |
| | 1 | 11.05 (1.09) Aa# | 11.78 (1.21) Aa |

Values followed by the different upper case letter in the same column or by different lower case letter in the same row are statistically different ($p < 0.05$). * and # represents statistical difference for DPI.

Water sorption and solubility

Table 5 shows the results of WS and S in $\mu\text{g}/\text{mm}^3$. The addition of DPI had higher WS values in cements containing 1 mol% CQ with 1 or 2 mol% EDAB. The EDAB concentration of 1 mol% produced lower values than 2 mol% EDAB when combined with 1 mol% CQ with or without DPI.

Solubility did not differ statistically ($p > 0.05$).

Table 5. Means (standard deviation) of Water Sorption and Solubility ($\mu\text{g}/\text{mm}^3$)

| DPI (mol%) | CQ (mol%) | Water sorption | | Solubility | |
|------------|-----------|------------------|------------------|-----------------|-----------------|
| | | EDAB (1 mol%) | EDAB (2 mol%) | EDAB (1 mol%) | EDAB (2 mol%) |
| 0 | 0.5 | 21.23 (4.70) Aa | 23.81 (4.12) Aa | -7.62 (2.61) Aa | -7.58 (2.32) Aa |
| | 1 | 14.01 (2.21) Bb* | 20.95 (4.83) Aa* | -3.33 (3.19) Aa | -5.71 (6.21) Aa |
| 0.5 | 0.5 | 26.67 (3.10) Aa | 22.38 (4.32) Ba | -2.86 (3.10) Aa | -2.38 (4.76) Aa |
| | 1 | 22.86 (3.19) Ab# | 29.39 (1.15) Aa# | -5.71 (3.19) Aa | -6.67 (2.61) Aa |

Values followed by the different upper case letter in the same column or by different lower case letter in the same row are statistically different ($p < 0.05$). * and # represents statistical difference for DPI.

Flexural strength and elastic modulus

Table 6 shows results for FS and E. The FS (MPa) and E (GPa) of the experimental resin cements tested did not differ statistically ($p > 0.05$).

Table 6. Means (standard deviations) of Flexural Strength (MPa) and Elastic Modulus (GPa).

| DPI (mol%) | CQ (mol%) | Flexural Strength | | Elastic Modulus | |
|------------|-----------|-------------------|----------------|-----------------|---------------|
| | | EDAB (1 mol%) | EDAB (2 mol%) | EDAB (1 mol%) | EDAB (2 mol%) |
| 0 | 0.5 | 125.69 (17.98) | 120.82 (23.21) | 3.39 (0.33) | 3.40 (0.28) |
| | 1 | 122.20 (9.88) | 127.03 (22.98) | 3.12 (0.28) | 3.20 (0.27) |
| 0.5 | 0.5 | 116.35 (17.26) | 121.39 (18.36) | 3.05 (0.35) | 3.37 (0.24) |
| | 1 | 109.96 (18.97) | 121.11 (15.12) | 3.24 (0.40) | 3.32 (0.25) |

Values followed by the different upper case letter in the same column or by different lower case letter in the same row are statistically different ($p < 0.05$). * and # represents statistical difference for DPI.

DISCUSSION

The present study investigated properties of experimental resin cements with different concentrations of EDAB, an aromatic tertiary amine, and CQ, a photosensitizer molecule. Although tertiary amines are prone to oxidation and can cause color changes, the yellowing effect can be also related to higher CQ concentrations in photoactivated materials^{7,12}. Thus, ideal luting materials must have as low concentrations as possible of these molecules without compromising properties in the polymer network.

DPI was added to this two-component system as a co-initiator forming a three-component photoinitiator system⁹. For DC, when the CQ concentration was reduced from 1 to 0.5 mol%, it was expected that properties would be negatively affected. Instead, in the cement containing 2 mol% EDAB, this was not observed on the DC when DPI was added, showing a positive effect of the salt even at lower CQ concentrations. Thus, the first hypothesis was partially rejected, because even with a higher concentration of components, not all properties were improved. Because of the known effectiveness of generating free radicals, DPI must contribute to more reactive bonds in the polymer formation, resulting in a high value of conversion^{10,13}. Therefore, even at low concentrations, the initiator systems containing DPI were capable of efficiently polymerizing the experimental resins^{9,10}.

However, when DPI was added to 1 mol% CQ, a decrease in DC was observed. Generally, the necessary concentration of amine:CQ is 2:1 or more in photoinitiator systems¹⁴. In the present study, the salt added to this system may have hindered the collision of molecules during the reaction because of its ionic nature and hydrophilic characteristics, which is in contrast to hydrophobic CQ and EDAB. A lower amine concentration can also make the exciplex formation more difficult to form, which explains why cements containing 1 mol% EDAB showed lower values than 2 mol% EDAB, indicating that the tertiary amine concentration directly affects the DC¹³.

Adding DPI as a third component may enable a small amount of CQ to be added into the model resin cement, and for this reason, the present study shows systems with 1 or 0.5 mol% CQ. This partial removal of CQ was intended to reduce the yellowing effect on coordinate b^* . The coordinates $L^*a^*b^*$ were individually analyzed and the second hypothesis was rejected, because adding the salt influenced the values. Adding DPI increased the L^* values in cement with 0.5 mol% CQ and 1 mol% EDAB, and this can be correlated to the color of the salt, which is a white powder. L^* values (Luminosity, from 0=black to 100=white) of around 80 indicate that all cements tested have a light color. DPI influenced coordinate a^* in cement with 1 mol% CQ and 1 mol% EDAB, decreasing the values. This influence was also demonstrated in another study that analyzed the composition with 0.5 mol% CQ/1 mol% EDAB/0.5 mol% DPI, where values around -2 were also found¹⁵. Considering the b^* axis, all cements with 0.5 mol% CQ were less yellow than 1 mol% CQ. Thus, the third hypothesis was accepted, because all formulations with a lower concentration of CQ presented lower values of b^* and, consequently, showed less yellowing effect. As is well known, CQ is a yellow powder and its potential to yellow the material must be considered when it is added⁷. Adding DPI was intended to compensate for the decrease in CQ concentration. In the present study, DPI increased b^* values only when combined with a 1:1 ratio of amine:CQ. Because of their double bonds, aromatic amines can react, creating higher energy states that could react with even oxygen or other aromatic groups, such as the salt radicals. These reactions may form color centers, as bigger conjugated systems in the polymer that lead to more visible light absorption in the blue region¹⁶. The DPI and EDAB reactions in these ways, or unreacted radicals, may be the cause of more yellowing in the cement containing the salt, which can also be related to the lower DC value

because of the 1:1 amine:CQ ratio. However, in 2 mol% EDAB, this influence was not observed because higher amounts of amine may have contributed to a higher DC, which can be correlated to the photodecomposition of CQ into colorless products, namely photobleaching¹⁷.

BisGMA/TEGDMA comonomer blends are capable of forming a heterogeneous polymeric structure with high cross-link density areas¹⁸. Because of its structural characteristics, TEGDMA causes formation of less homogeneous copolymers. Even in cross-link bond areas, microgel domains may be the result of free radical polymerization of dimethacrylates. These areas with unreacted monomers can present hydrogen bonds between $>C=O$ and $-O-$ of TEGDMA with $-OH-$ groups of BisGMA in the spaces between the chains formed¹⁹. These polar groups can explain how the process of sorption in the present study occurred, considering the water molecule as a polar structure that could easily be diffused in a polymer. Another factor is that the ionic nature of DPI as a salt can lead the polymer to absorb more water¹³.

The hydrophilic character of DPI molecules and the polar groups of the base comonomer blend may have contributed to allowing more water into the tested resin cements that contained DPI. The lower WS values in cement with 1 mol% EDAB was obtained with 1 mol% CQ. Despite the lower DC for 1 mol% EDAB, the combination with 1 mol% CQ may have formed a more stable polymer cross-link structure, with less pendant polar groups, especially without the addition of hydrophilic DPI. WS is a poor predictor of DC because even in high cross-linked polymers, the process of water diffusion is highly dependent upon the chemistry of monomers²⁰.

In this study, all WS and S results were acceptable, considering that ISO establishes $\leq 40 \mu\text{g}/\text{mm}^3$ and $\leq 7.5 \mu\text{g}/\text{mm}^3$, respectively, as the maximum values to accomplish the requirements. The present results are also consistent with those of previous studies demonstrating similar values for WS in other resin cements tested²¹. Negative values in solubility may suggest an increase in the polymer mass because of the difficulty of removing water in the final process of the test²². In addition to the solubility test, flexural strength and elastic modulus showed that even with a variation in components, the polymer network achieved a similar behavior, showing no statistical differences in the results. The 60% filler mass fraction may have contributed to values that were higher than the 50 MPa reported in other studies^{23,24}. This value is established as a minimum acceptable value for FS in Type 1, Class 2 materials, ISO 4049/2009 requirements. The present study showed the influence of adding DPI and reducing CQ in ternary initiator systems and its effects on the yellowing reduction and adequate property maintenance. Thus, future investigations are needed to determine suitable photoactivation times and their relationship to the indirect restoration's thickness, as well as the behavior of color properties as a function of time.

Within the limitations of this study, it can be concluded that the best formulation tested in this study was the cement with 0.5 mol% CQ / 2 mol% EDAB / 0.5 mol% DPI, which provided an adequate DC and sorption with a reduced yellowing effect. Additionally, the compensatory effect of DPI for reducing the CQ concentration is more effective with 2 mol% EDAB.

Acknowledgments

This work was supported by Amazonas Research Foundation (FAPEAM) – Grant number 005/2012 – Decision 269/2012.

REFERENCES

1. Hoorizad Ganjkar M, Heshmat H, Hassan Ahangari R. Evaluation of the Effect of Porcelain Laminate Thickness on Degree of Conversion of Light Cure and Dual Cure Resin Cements Using FTIR. *J Dent (Shiraz)*. 2017 Mar;18(1):30-6.
2. Jang Y, Ferracane JL, Pfeifer CS, Park JW, Shin Y, Roh BD. Effect of Insufficient Light Exposure on Polymerization Kinetics of Conventional and Self-adhesive Dual-cure Resin Cements. *Oper Dent*. 2017 Jan/Feb;42(1):E1-E9. doi: 10.2341/15-278-L.
3. Archegas LR, Freire A, Vieira S, Caldas DB, Souza EM. Colour stability and opacity of resin cements and flowable composites for ceramic veneer luting after accelerated ageing. *J Dent*. 2011 Nov;39(11):804-10. doi: 10.1016/j.jdent.2011.08.013.
4. Stansbury JW. Curing dental resins and composites by photopolymerization. *J Esthet Dent*. 2000;12(6):300-8.
5. Ilie N, Hickel R. Can CQ be completely replaced by alternative initiators in dental adhesives? *Dent Mater J*. 2008 Mar;27(2):221-8.
6. Brandt WC, Tomaselli L de O, Correr-Sobrinho L, Sinhoreti MA. Can phenyl-propanedione influence Knoop hardness, rate of polymerization and bond strength of resin composite restorations? *J Dent*. 2011 Jun;39(6):438-47. doi: 10.1016/j.jdent.2011.03.009.
7. de Oliveira DC, Rocha MG, Gatti A, Correr AB, Ferracane JL, Sinhoreti MA. Effect of different photoinitiators and reducing agents on cure efficiency and color stability of resin-based composites using different LED wavelengths. *J Dent*. 2015 Dec;43(12):1565-72. doi: 10.1016/j.jdent.2015.08.015.
8. Emami N, Söderholm KJ. Influence of light-curing procedures and photo-initiator/co-initiator composition on the degree of conversion of light-curing resins. *J Mater Sci Mater Med*. 2005 Jan;16(1):47-52.
9. Gonçalves LS, Morães RR, Ogliari FA, Boaro L, Braga RR, Consani S. Improved polymerization efficiency of methacrylate-based cements containing an iodonium salt. *Dent Mater*. 2013 Dec;29(12):1251-5. doi: 10.1016/j.dental.2013.09.010.
10. Ogliari FA, Ely C, Petzhold CL, Demarco FF, Piva E. Onium salt improves the polymerization kinetics in an experimental dental adhesive resin. *J Dent*. 2007 Jul;35(7):583-7.
11. Crivello JV, Lam JH. Diaryliodonium salts – new class of photo-initiators for cationic polymerization. *Macromolecules*. 1977 Nov;10(6):1307-15.
12. Schneider LF, Cavalcante LM, Consani S, Ferracane JL. Effect of co-initiator ratio on the polymer properties of experimental resin composites formulated with camphorquinone and phenyl-propanedione. *Dent Mater*. 2009 Mar;25(3):369-75. doi: 10.1016/j.dental.2008.08.003.
13. Guo X, Wang Y, Spencer P, Ye Q, Yao X. Effects of water content and initiator composition on photopolymerization of a model BisGMA/HEMA resin. *Dent Mater*. 2008 Jun; 24(6):824-31.
14. Andrade KM, Palialol AR, Lancellotti AC, Aguiar FH, Watts DC, Gonçalves LS, et al. Effect of diphenyliodonium hexafluorophosphate on resin cements containing different concentrations of ethyl 4-(dimethylamino)benzoate and 2-(dimethylamino)ethyl methacrylate as co-initiators. *Dent Mater*. 2016 Jun;32(6):749-55. doi: 10.1016/j.dental.2016.03.014.

15. Albuquerque PP, Bertolo ML, Cavalcante LM, Pfeifer C, Schneider LF. Degree of conversion, depth of cure, and color stability of experimental dental composite formulated with camphorquinone and phenanthrenequinone photoinitiators. *J Esthet Restor Dent*. 2015 Mar-Apr;27 Suppl 1:S49-57. doi: 10.1111/jerd.12131.
16. Furuse AY, Mondelli J, Watts DC. Network structures of Bis-MA/TEGDMA resins differ in DC, shrinkage-strain, hardness and optical properties as a function of reducing agent. *Dent Mater*. 2011 May;27(5):497-506. doi: 10.1016/j.dental.2011.02.007.
17. Asmusen S, Arenas G, Cook WD, Vallo C. Photobleaching of camphorquinone during polymerization of dimethacrylate-based resins. *Dent Mater*. 2009 Dec;25(12):1603-11. doi: 10.1016/j.dental.2009.08.010.
18. Ferracane JL. Resin composite--state of the art. *Dent Mater*. 2011 Jan;27(1):29-38. doi: 10.1016/j.dental.2010.10.020.
19. Sideridou I, Tserki V, Papanastasiou G. Study of water sorption, solubility and modulus of elasticity of light-cured dimethacrylate-based dental resins. *Biomaterials*. 2003 Feb;24(4):655-65.
20. Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. *Dent Mater*. 2006 Mar;22(3):211-22.
21. Mese A, Burrow MF, Tyas MJ. Sorption and solubility of luting cements in different solutions. *Dent Mater J*. 2008 Sep;27(5):702-9.
22. Janda R, Roulet JF, Latta M, Rüttermann S. Water sorption and solubility of contemporary resin-based filling materials. *J Biomed Mater Res B Appl Biomater*. 2007 Aug;82(2):545-51.
23. Kim KH, Ong JL, Okuno O. The effect of filler loading and morphology on the mechanical properties of contemporary composites. *J Prosthet Dent*. 2002 Jun;87(6):642-9.
24. Gonçalves F, Azevedo CL, Ferracane JL, Braga RR. BisGMA/TEGDMA ratio and filler content effects on shrinkage stress. *Dent Mater*. 2011 Jun;27(6):520-6. doi: 10.1016/j.dental.2011.01.007.