

Achieving property enhancements in dental resin composites via reduced concentrations of camphorquinone within a ternary initiator system

Dressano, Diogo; Salvador, Marcos Vinícius Oliveira; Aguiar, Flávio Henrique Baggio; Gonçalves, Luciano Souza; Palin, William M.; Watts, David C.; Hadis, Mohammed A.; Lima, Adriano Fonseca; Marchi, Giselle Maria

DOI:

[10.1016/j.dental.2024.06.022](https://doi.org/10.1016/j.dental.2024.06.022)

[10.1016/j.dental.2024.06.022](https://doi.org/10.1016/j.dental.2024.06.022)

License:

Creative Commons: Attribution (CC BY)

Document Version

Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Dressano, D, Salvador, MVO, Aguiar, FHB, Gonçalves, LS, Palin, WM, Watts, DC, Hadis, MA, Lima, AF & Marchi, GM 2024, 'Achieving property enhancements in dental resin composites via reduced concentrations of camphorquinone within a ternary initiator system', *Dental Materials*, vol. 40, no. 9, pp. 1400-1408. <https://doi.org/10.1016/j.dental.2024.06.022>, <https://doi.org/10.1016/j.dental.2024.06.022>

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.



Achieving property enhancements in dental resin composites via reduced concentrations of camphorquinone within a ternary initiator system

Diogo Dressano^a, Marcos Vinícius Oliveira Salvador^b, Flávio Henrique Baggio Aguiar^a, Luciano Souza Gonçalves^c, William M. Palin^d, David C. Watts^e, Mohammed A. Hadis^{d,*}, Adriano Fonseca Lima^{b,**}, Giselle Maria Marchi^a

^a Department of Restorative Dentistry, Piracicaba Dental School, State University of Campinas, Av Limeira, 901 Mail Box 52, Piracicaba, Sao Paulo 13414-903, Brazil

^b Dental Research Division, Paulista University, Rua Doutor Bacelar, 1212, CEP: 04026-002 Sao Paulo, Brazil

^c Department of Restorative Dentistry, School of Dentistry, Federal University of Santa Maria, Av. Roraima, 1000 - Camobi, Santa Maria, RS 97105-900, Brazil

^d University of Birmingham, College of Medical and Dental Sciences, Institute of Clinical Sciences, 5 Mill Pool Way, Edgbaston, Birmingham B5 7EG, UK

^e School of Medical Sciences and Photon Science Institute, Coupland 3 Building, University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom

ARTICLE INFO

Keywords:

Photoinitiator
Camphorquinone
Iodonium salt
DPI
Light transmission

ABSTRACT

Objectives: The study aimed to assess the impact of diphenyliodonium hexafluorophosphate (DPI) on the physicochemical properties of experimental resin composites (ECRs) featuring reduced concentrations of camphorquinone (CQ)/amine.

Methods: Five concentrations of CQ (0.125, 0.25, 0.5, 0.75, and 1 mol%) with dimethylaminoethyl amine benzoate (EDAB) in a 1:2 mol% ratio (CQ:EDAB) were incorporated into a 50:50 mass% monomer blend of bisphenol glycidyl methacrylate (BisGMA) and triethyleneglycol dimethacrylate (TEGDMA). An additional 5 groups with the same CQ:EDAB concentrations had 0.5 mol% DPI added. Each resin group contained 60 wt% of 0.7 μm barium-alumino-silicate glass. Light transmission (n = 3), real-time degree of polymerization (n = 3), temperature change during polymerization (n = 5), polymerization shrinkage strain (n = 3), flexural strength, and modulus (n = 12), as well as water sorption and solubility (n = 5), were evaluated. Data were analyzed using two-way ANOVA and Tukey's post-hoc test ($\alpha = 0.05$).

Results: Light transmission was reduced in groups containing 0.125 and 0.25 mol% of CQ without DPI. DPI increased temperature, degree and rate of polymerization, despite the reduction in CQ/amine concentration. Additionally, there was an increase in polymerization shrinkage strain, flexural strength and modulus, and a reduction in water sorption and solubility in ECRs with DPI, even with lower concentrations of CQ/EDAB.

Significance: DPI improved the assessed properties of composites across various concentrations of CQ/EDAB, showing the benefit of reducing the quantity of CQ used without compromising the properties and curing of the resin composites.

1. Introduction

Camphorquinone (CQ) is a photosensitizer commonly used in light-curing resin dental materials, with an absorption peak around 470 nm [1,2]. Such Type II photosensitizers require a co-initiator, typically a tertiary amine, to initiate polymerization [1,3]. Upon light irradiation, CQ can form two excited states: a singlet state, which plays a minor role in the polymerization process, and a triplet state, crucial for the generation of free radicals. Upon reaction with the amine, CQ forms an

exciplex, abstracting hydrogen from the tertiary amine to produce an unreactive CQ-cetyl radical and a N-N aminyl radical, which does initiate polymerization [1,4].

Camphorquinone (CQ) is a yellow compound, so an excessive concentration will influence the color of the resin, particularly in lighter-shade resin composites. However, it has reduced efficiency in polymerization initiation compared with alternative photoinitiators like monoacylphosphine oxide (MAPO) and phenylbis (2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO), but allows improved light

* Corresponding author.

** Correspondence to: Dental Research Division, School of Dentistry – Paulista University, Rua Doutor Bacelar, 1212, CEP: 04026-002 Sao Paulo, Brazil.

E-mail addresses: M.Hadis@bham.ac.uk (M.A. Hadis), lima.adf@gmail.com (A.F. Lima).

<https://doi.org/10.1016/j.dental.2024.06.022>

Received 30 April 2024; Received in revised form 14 June 2024; Accepted 14 June 2024

Available online 22 June 2024

0109-5641/© 2024 The Author(s). Published by Elsevier Inc. on behalf of The Academy of Dental Materials. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

transmittance due to its lower molar absorptivity [5,6] and longer irradiating wavelengths. Higher transmittance is advantageous for restorative composites, particularly bulk-fill materials. Moreover, alternative photoinitiators such as MAPO and BAPO absorb light in the shorter-wavelength violet region (approximately 410 nm) compared with the blue region (around 470 nm) required by CQ. Consequently, broad band light sources are necessary when using these alternative photoinitiators.

Achieving a high degree of polymerization is crucial to ensure that dental materials possess the necessary physical properties (i.e. water sorption, solubility, flexural strength and modulus) to withstand oral challenges such as mastication forces and high humidity. Changes in the initiator system, such as use of different photoinitiators [2,7,8], the type of co-initiator used [3,9] and changes in the sensitizer/co-initiator ratio [3] can significantly influence the polymerization reaction, leading to alterations in the material's physical and chemical properties. For instance, an increase in system reactivity may result in higher resin polymerization shrinkage [10], which can directly influence on the shrinkage stress promoted in the tooth structure when considering the dental restorative composites [11].

Previous studies demonstrated that the use of iodonium salts is a feasible alternative to improve the polymerization and physical properties of resins using CQ as photosensitizer [2,3,10,12–16], also showing the efficacy of iodonium salts in increasing the rate and degree of conversion of resin materials, achieving similar results to alternative initiators like MAPO and BAPO [2]. The mechanism of ternary photoinitiators containing iodonium salts involves an irreversible electron transfer from the CQ ketyl or amine to the iodonium salt. The iodonium salt then rapidly fragment into a molecule of phenyl iodide and a phenyl radical. These irreversible reactions regenerate the CQ molecule and convert the amine radical into a carbo-cation. The increased efficiency in such systems is due 1) consumption of the inactive terminating ketyl radical through oxidation by the iodonium salt which yields an additional phenyl radical that is active for initiation and 2) inhibition of 'back-electron transfer' processes due to the presence of iodonium salts.

Whilst the presence of iodonium salts improves efficiency, previous studies [2,3,10,12–16] evaluated resins containing amounts ca. 0.5–1 % wt of CQ, which are concentrations with proven efficiency of polymerization initiation even without the use of an iodonium salt. Based on this, the incorporation of an iodonium salt could be a promising approach to reducing the amount of CQ used in dental resins without compromising the final properties of the material. Therefore, the present study evaluated the use of an iodonium salt, within resins containing reduced concentrations of CQ, to demonstrate its efficiency (i) not only by improving the degree of conversion of the dental resin composites, but also (ii) its influence on others chemical and physical properties. The objectives were to assess the influence of iodonium salts on key properties of model dental resin composites with decreasing concentrations of CQ. These critical properties include: light transmission, degree of conversion, rate of polymerization, temperature change, polymerization shrinkage, flexural strength and modulus, water sorption and solubility.

2. Materials and methods

2.1. Experimental material composition

Experimental resin composites (ERCs) were formulated using Bisphenol A diglycidyl dimethacrylate (Bis-GMA; Esstech, Essington, PA, USA) and tri-ethylene glycol dimethacrylate (TEGDMA; Esstech) at a 50:50 mass ratio and filled to 60 wt% with Barium Borosilicate glass 0.7 μm , density 3.0 g/mL, refractive index 1.553, (V117 4107, Esstech), using a mechanical mixer (DAC 150 Speedmixer, Flacktek, Landrum, SC, USA) for 5 min at 2400 rpm.

The experimental groups (Table 1) were established varying the concentration of camphorquinone (CQ, Sigma–Aldrich Inc., St. Louis,

Table 1

Experimental groups established according to the polymerisation initiator system. *For DPI, 0.5 mol% is equal to 0.65 wt%.

Group	[CQ] mol%	[CQ] wt %	[EDAB] mol%	[EDAB] wt %	[DPI] mol %*
G1	0.125	0.0625	0.25	0.125	————
G2	0.250	0.1250	0.50	0.250	————
G3	0.500	0.2500	1.00	0.500	————
G4	0.750	0.3750	1.50	0.750	————
G5	1.000	0.5000	2.00	1.000	————
G6	0.125	0.0625	0.25	0.125	0.5
G7	0.250	0.1250	0.50	0.250	0.5
G8	0.500	0.2500	1.00	0.500	0.5
G9	0.750	0.3750	1.50	0.750	0.5
G10	1.000	0.5000	2.00 mol%	1.000	0.5

MO, USA) (0.125, 0.25, 0.5, 0.75, and 1 mol%) and with or without 0.5 mol% diphenyliodonium hexafluorophosphate (DPI, Sigma–Aldrich Inc., St. Louis, MO, USA). The amine (ethyl-4-dimethylamino benzoate-EDAB, Sigma–Aldrich Inc., St. Louis, MO, USA) was used in the same proportion 1:2 mol% (CQ/amine) for all groups. All procedures were carried out under yellow lights to prevent inadvertent curing.

For all analyses, the light-curing was performed using a light-emitting diode (LED, Bluephase G2, Ivoclar-Vivadent, Schaan, Liechtenstein), with a mean irradiance of 1147 mW/cm² measured using a spectrophotometer (MARC™; Bluelight Analytics Inc., Halifax, Canada).

2.2. Light transmission

A mylar strip was positioned over the cosine corrector of a spectrophotometer (MARC™; Bluelight Analytics Inc., Halifax, Canada), and then a silicone mold (8 mm diameter, 1 mm thickness) were positioned centralized to the one. A baseline measurement of irradiance was taken, without resin interposing, before the measurement of the light transmission through the resin. ERCs specimens were inserted in the mold, and a microscope cover slip (0.1 mm thickness) was placed over the upper surface. The transmitted irradiance through the resin composites was measured during polymerisation (30 s) and analysed in real-time (n = 3), with the LED tip positioned in contact with the cover slip. The transmitted irradiance was analysed and recorded via system software (MARC-RC, Halifax, Canada).

2.3. Real-time degree of polymerisation

A Fourier transform infrared spectrometer with an attenuated total reflectance (ATR) (FTIR-ATR, Nicolet 6700, Thermo Scientific, Pittsburgh, PA, USA) method was used to measure the ERC degrees of conversion (DC). A reproducible specimen dimension was obtained by fixing a silicon mold (8 mm diameter, 1 mm thick) onto the ATR plate (Thermo Fisher, Smart MIRacle Diamond ATR, Waltham, Massachusetts, United States) with concentric alignment to the ATR diamond. The mold was filled with the experimental resin composite and the upper surface was covered with a 0.1 mm glass cover slip. Real-time DC (120 s) was measured using aliphatic (1638 cm⁻¹) and aromatic (1608 cm⁻¹) C=C absorption at the lower surface (3 scans averaged per spectrum, 16 cm⁻¹ resolution). The specimens (n = 3) were light-cured for 40 s and DC was calculated according to Eq. 1:

$$\text{Conversion\%} = 1 - \frac{\text{aliphatic/isosbestic (peak areas of polymer)}}{\text{aromatic/isosbestic (peak areas of monomer)}} \times 100 \quad (1)$$

The rate of polymerisation was calculated as the derivative of the degree of conversion versus time.

2.4. Temperature changes during polymerisation

The variation of temperature during the polymerisation was measured in a room with controlled ambient temperature (23 ± 2 °C), using a K-type thermocouple (1 mm diameter) connected to a digital display (Iopetherm 46, IOPE, São Paulo), with an accuracy of 0.1 °C. The thermocouple was inserted laterally into a silicone matrix (5 mm diameter, 3 mm height), with the tip in contact with the resin material 1 mm below the top surface. The silicone matrix was filled with each ERC ($n = 5$) and light-cured for 40 s. Temperature change was monitored for a duration of 180 s, allowing ample time for the resin temperature to equilibrate with the room temperature. After this, a second light activation was performed on the same cured specimen, aiming to obtain the temperature increase promoted by the light emitted by the LCU. Temperature (°C) within the increment was recorded every second. The temperature change results for each resin were derived by subtracting the temperature change prompted by the LCU from those observed at the moment of resin polymerization. The mean maximum temperature for each group was calculated, providing an overview of the thermal dynamics during the polymerization process.

2.5. Polymerisation shrinkage strain

The 'Bonded Disk' method was used to measure polymerisation strain, as developed by Watts et al. [17]. Disk-shaped specimens were prepared (8 mm diameter, 1 mm thick) using a matrix centrally positioned upon a rigid glass plate (3 mm thick). A highly compliant glass sheet ($22 \text{ mm}^2 \pm 0.1$ mm thick) was positioned resting on the upper surface of the specimen.

Before polymerisation, the device tip of a linear variable differential transducer (LVDT, Type GT 2000, RDP Electronics, Wolverhampton, UK) was positioned above the specimen centre in contact with the coverslip. The LED light-curing unit tip was fixed beneath and centred relative to the specimen for light delivery upwards and through the glass plate. Real-time measurements ($n = 3$) were started 20 s before light irradiation (40 s) to provide a baseline LVDT output signal. Shrinkage strain were continuously measured for 20 min following light irradiation. The rate and maximum shrinkage strain of each specimen were obtained, followed by statistical analysis. The rate of shrinkage was calculated as the derivative of shrinkage *versus* time.

2.6. Flexural strength (FS) and modulus (E)

For three-point bending measurements, bar-shaped specimens (25 mm length, 2 mm width, 2 mm height) were prepared ($n = 10$) using a stainless steel mold. The matrix was positioned on a glass plate and then filled with the experimental resin composites, with a glass slide (0.1 mm thick) placed above the resin before curing. The tip of LCU was positioned centrally and flat against the axis of the bar to polymerise the specimens, with five successive overlapping steps (5×40 s irradiations) originating from the centre of the specimen.

The specimen dimensions were measured before testing using a digital calliper (Mitutoyo, Tokyo, Japan) accurate to 0.01 mm. Then, a three-point bending test was performed with a universal testing machine (2000RK, Kratos, São Paulo, Brazil) at a 1 mm/min crosshead speed (distance between the supports – 20 mm). The flexural strength (FS) was calculated according to Eq. 2:

$$FS = \frac{3FI}{2bh^2} \quad (2)$$

"F" = maximum load (Newtons) required to break the specimen

"l" = the distance between supports (20 mm)

"b" = the average specimen width and "h" the average thickness.

The flexural modulus (E) for each sample was calculated from the

linear portion of the stress-strain curve, corresponding to the elastic deformation of the material, using Eq. 3:

$$E = \frac{\Delta F}{\Delta Y} \times \frac{l^3}{4bh^3} \quad (3)$$

$\Delta F / \Delta Y$ = force change (ΔF) per unit change in deflection (ΔY) at the centre of the specimen.

L = distance between supports (20 mm);

b = average specimen width.

h = average thickness.

2.7. Water Sorption and solubility

Water sorption and solubility measurements were performed according to ISO 4049–2009, except for the specimen size (5 mm diameter, 1 mm thick), which was reduced to allow light curing in a single step, and with the period of 21 days for water immersion. Discs were prepared using silicone molds.

After curing, the specimens ($n = 5$) were stored in plastic tubes in a desiccator at 37 °C. The specimens were weighed daily using an analytical balance during the drying period until constant mass (m_1) was obtained where the variation between three successive weights was lower than ± 0.001 g. The initial diameter and thickness were measured using a digital calliper to calculate the sample volume (mm^3) at four equidistant points. After obtaining m_1 , the specimens were immersed in 1.5 mL of distilled water and stored at 37 °C for 21 days.

After being immersed in water, the specimens were lightly dried using absorbent paper and weighed to obtain the mass after immersion in water (m_2). After this, the specimens were again placed in a desiccator at 37 °C, to obtain the final dry mass. The specimens were weighed daily until a constant weight (m_3) was obtained. The sorption values and solubility were calculated in g/mm^3 by the following formulae:

$$\text{Sorption} = \frac{(m_2 - m_3)}{V} \quad (4)$$

$$\text{Solubility} = \frac{(m_1 - m_3)}{V} \quad (5)$$

m_1 = initial weight before immersion in distilled water (mg);

m_2 = mass after immersion in distilled water (mg);

m_3 = mass after the second drying cycle (mg);

V = volume of the m_1 specimen (mm^3).

2.8. Statistical analysis

Normality tests were performed and homogeneity of variances analysed, and then Two-way Analysis of Variance (ANOVA) was applied for comparison of experimental groups, considering "CQ concentration" and "iodonium salt" as main factors. For comparison among groups in all evaluations, Tukey's test was performed. All analyses were carried out at a 5 % significance level.

3. Results

3.1. Light transmission

ERCs with higher concentrations of CQ (0.75 and 1 mol%) showed reduced light transmission during the initial seconds with a plateau in irradiance (ca. 450 mW/cm^2) reached at ca. 25 s. For the lower concentrations (0.25 CQ and 0.125 CQ), the initial light transmission was higher than the other groups but the final transmission at the end of the measurement was significantly lower ($p < 0.001$) and no plateau was observed. ERCs without DPI stabilised the light transmission between 390 and 500 mW/cm^2 after 25 s (Fig. 1A). However, all composites containing DPI reached the light transmission plateau (ca. 450 $\text{mW}/$

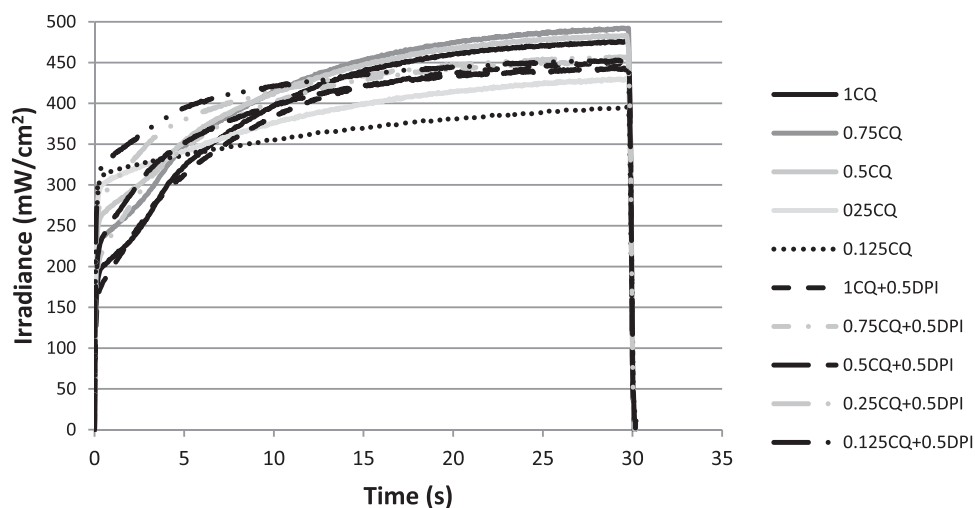


Fig. 1. Light transmission through ERCs ($n = 3$). A consistent pattern was observed across all composites, with light transmission increasing in accordance with polymerization progression. Notably, 0.125 CQ with and without DPI exhibited higher light transmission initially, possibly attributable to the reduced amount of CQ.

cm^2) at ca. 20 s irradiation (Fig. 1B). The resin composites containing DPI had similar light transmission. For composites containing 0.5, 0.75 and 1 mol% CQ, the absence of DPI provided increased light transmission (Table 2).

3.2. Degree of conversion and polymerisation rate

According to the statistical analysis, there was a highly significant effect of each independent factors (CQ/Amine concentration $p < 0.0001$; iodonium salt $p < 0.0001$), and also there was a highly significant interaction ($p < 0.0001$) between factors ("DPI" and "CQ/Amine concentration") for both the degree of conversion (after 120 s) and the maximum polymerisation rate. The groups containing 0.5 and 0.75 mol% of CQ showed no statistical difference between the groups with and without DPI (Table 2, Fig. 2). The highest degree of conversion was obtained by the resin containing 1 mol% CQ plus DPI. ERCs with 0.5 mol%, 0.75 mol% and 1 mol% of CQ without DPI showed a collectively similar degree of conversion. The ERC with a concentration of 0.125 mol% without DPI showed the lowest DC of all evaluated composites.

All ERCs containing DPI had an increased polymerisation rate compared to their no-salt equivalents (Fig. 3). The polymerisation rate of composites containing 0.125 and 0.25 mol% CQ with DPI was 2x greater than the same resin without DPI. The materials containing 0.75 mol% and 1 mol% of CQ associated with DPI had the highest polymerisation rate, while the group containing 0.125 mol% of CQ without DPI had the lowest result in this evaluation. For both situations (with and without DPI), increasing the concentration of CQ promoted an increase in the polymerisation rate.

Different behaviour was observed for ERCs with and without DPI (Fig. 3). While composites with DPI showed a well-defined acceleration peak just after 2 s of activation, followed by a deceleration soon after. Composites without DPI showed a slower and longer reaction than ERCs containing the iodonium salt until the a plateau in properties was reached.

3.3. Real-time polymerisation temperature

The interaction between the factors was observed for the temperature change analysis of the polymerisation reaction. For the groups with and without DPI, the lowest temperature increases were observed in those containing 0.125 mol% of CQ (Table 2). The groups containing 0.5, 0.75, and 1 mol% of CQ presented related results, and the group containing 0.25 mol% of CQ presented intermediate results. The

addition of DPI to the resins promoted an increase in temperature during polymerisation for all tested concentrations compared to the ERCs without DPI.

3.4. Real-time shrinkage strain

For the maximum shrinkage strain and rate, an interaction was observed among the analysed factors. The use of DPI generated more significant shrinkage strain for all ERCs (Table 2, Fig. 4). ERCs with 0.125 mol% of CQ showed less shrinkage. For composites without DPI, all materials had the same shrinkage, except for the concentration of 0.125 mol%. As for the ERCs containing DPI, the concentration of 1 mol% promoted greater shrinkage, with intermediate values found at concentrations 0.75; 0.5, and 0.25 mol%.

Regarding the maximum contraction rate, the increase in this property followed the increase in the CQ concentration (Fig. 5). As noted for maximum shrinkage, all ERCs containing DPI had a higher shrinkage rate than those without DPI.

3.5. Flexural strength and elastic modulus

The presence of DPI increased flexural strength for all ERCs compared to formulations without salt (Fig. 6). When the CQ concentrations were compared, the composites with 0.125 mol% of CQ had the lowest flexural strengths for the groups with and without DPI, and the other concentrations had comparable results.

Although DPI has also positively influenced the flexural strengths of ERCs, only materials containing 0.25 mol% and 0.125 mol% of CQ were statistically superior to those without salt for ME. For the other concentrations (0.5, 0.75, and 1 mol%), the ERCs showed similar results, regardless of the presence of DPI.

3.6. Water sorption and solubility

In general, composites with CQ concentrations starting at 0.5 mol% showed lower water sorption regardless of the addition of DPI (Fig. 7). The groups containing 0.125 mol% and 0.25 mol% of CQ presented the highest sorptions, differing from the others. Except for the groups containing 0.125 and 0.5 mol% of CQ, which showed greater water sorption in composites without DPI than those containing the iodonium salt, all other groups with and without DPI presented comparable results in water sorption.

Regarding solubility, resins without DPI containing 0.125 and 0.25 mol% presented the highest solubilities and were also statistically

Table 2

Means and (standard deviations) of light transmission (n = 3), degree of conversion and rate of polymerization (n = 5), maximum shrinkage and maximum rate of shrinkage (n = 3).

Light Transmission After 30 s (mW/cm ²)		
[CQ] (mol%)	0 mol% DPI	DPI 0.5 mol%
0.125	396.2 (6.7) Bc	454.6 (8.2) Aa
0.25	431.9 (8.1) Bb	458.6 (0.5) Aa
0.5	484.36 (8.4) Aa	444.2 (8.5) Ba
0.75	493.1 (4.1) Aa	453.3 (2.7) Ba
1	477.5 (14.7) Aa	450.9 (3.4) Ba
Degree of Conversion 120 s (%)		
CQ [] (mol%)	Absence of DPI	DPI 0.5 mol%
0.125	62.87 (0.55) Bc	68.65 (0.29) Ad
0.25	68.73 (0.44) Bb	71.12 (0.59) Ac
0.5	72.59 (0.25) Aa	72.1 (0.5) Abc
0.75	73.89 (0.34) Aa	72.3 (0.27) Ab
1	73.14 (1.04) Aa	74.79 (0.42) Aa
Maximum Rate of Polymerisation (%/s)		
CQ [] (mol%)	Absence of DPI	DPI 0.5 mol%
0.125	4.93 (0.42) Bd	13.14 (0.74) Ad
0.25	7.09 (0.66) Bc	16.53 (0.89) Ac
0.5	10.6 (0.46) Bb	18.51 (0.35) Ab
0.75	12.17 (0.43) Ba	19.57 (0.41) Aab
1	13.77 (1.7) Ba	20.75 (0.18) Aa
Max Temperature (°C)		
CQ [] (mol%)	Absence of DPI	DPI 0.5 mol%
0.125	2,0 (1,09) Bc	10,4 (1,01) Ac
0.25	6,2 (1,16) Bb	14,8 (1,72) Ab
0.5	12,25 (2,48) Ba	17,6 (2,49) Aa
0.75	11,4 (1,35) Ba	18,2 (1,16) Aa
1	14,2 (1,32) Ba	18,4 (2,24) Aa
Max Shrinkage Strain (%)		
CQ [] (mol%)	Absence of DPI	DPI 0.5 mol%
0.125	4.54 (0.15) Bb	4.92 (0.03) Ac
0.25	5.01 (0.15) Ba	5.49 (0.02) Ab
0.5	5.22 (0.07) Ba	5.55 (0.11) Ab
0.75	5.3 (0.06) Ba	5.68 (0.19) Ab
1	5.22 (0.03) Ba	6.03 (0.02) Aa
Max Rate of Shrinkage (%/s)		
CQ [] (mol%)	Absence of DPI	DPI 0.5 mol%
0.125	0.18 (0.003) Be	0.64 (0.01) Ad
0.25	0.33 (0.003) Bd	0.88 (0.02) Ac
0.5	0.57 (0.04) Bc	1.05 (0.01) Ab
0.75	0.66 (0.01) Bb	1.08 (0.03) Ab
1	0.74 (0.01) Ba	1.15 (0.02) Aa

Different letters indicate statistical differences. Capital letters compare DPI presence (across) and lower case letters compare different amount of CQ (down). Two-way ANOVA and Tukey's test ($\alpha = 0.05$).

higher compared to composites with the same concentration of CQ containing DPI. For composites containing DPI, the concentration of 0.125 mol% showed the highest solubility.

4. Discussion

The current investigation highlights the complex relationship between the components of the photoinitiator system including concentration and the presence of DPI on properties of dental resin composites. Notably, it becomes evident that both factors ("presence of DPI" and "CQ concentrations") impact light transmission through the resin. Specifically, lower CQ concentrations (0.125 and 0.25 mol%) in ERCs exhibited heightened light transmission during the initial seconds of photoactivation, likely attributed to the reduced yellowing by reduced CQ concentration. However, as polymerization progressed, ERCs lacking DPI and containing lower CQ concentrations (0.125 and 0.25 mol%) demonstrated diminished light transmission after 30 s compared with

those with higher CQ concentrations (greater than 0.5 mol%). This phenomenon can be attributed to the consumption of photoinitiators during polymerization, leading to an increase in light transmission within the composite [5,6,18]. Moreover, the large RI mismatch between the refractive index of the resin and fillers (Resin RI ~1.50; Filler RI is ~1.55) probably caused interfacial scattering [18,19]. At the beginning of the measurements, the RI mismatch was the same in all groups and therefore the initial differences ($t = 0$) in light transmission are likely due to the differences in CQ concentration according to Beer-Lamberts Law. As polymerisation proceeds, the material-light interaction becomes more complex, involving shrinkage, refractive index change and temperature [18,19]. These dynamic processes are likely to depend on the photoinitiator type and concentration resulting in differences in rates of polymerisation and the final degree of conversion (Figs. 2 and 3). However, composites containing 0.5, 0.75, and 1 mol% of CQ combined with DPI exhibited higher polymerization rates, significantly lower light transmission following 30 s irradiation,

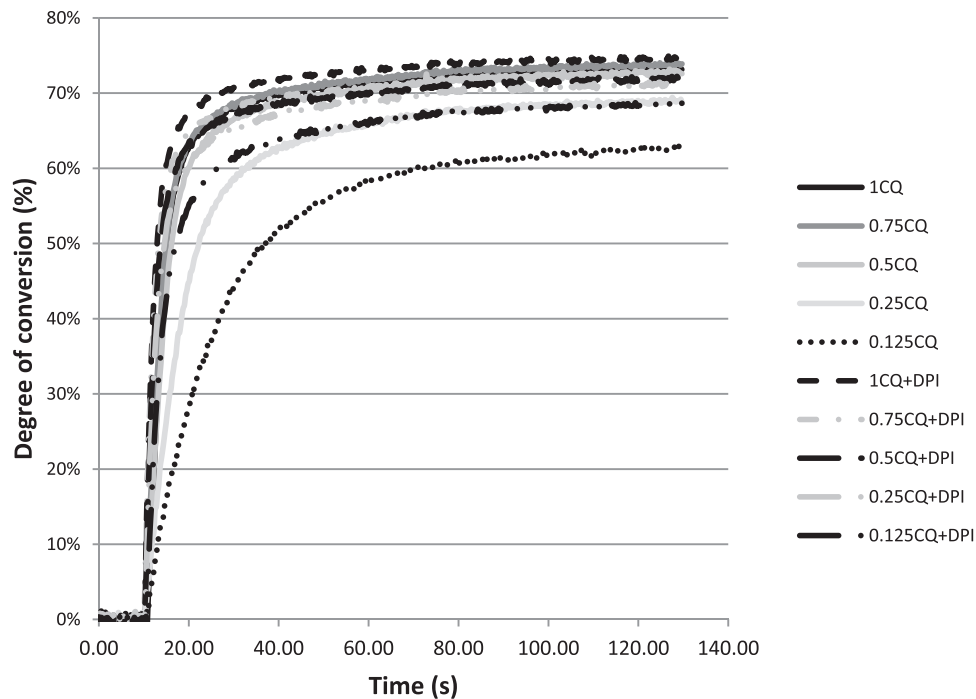


Fig. 2. Real-time degree of conversion (%; $n = 5$) of ERCs. The figure highlights the lower degree of conversion of 0.125 C Q without DPI compared to the other composites. The first ten seconds were used as a baseline without irradiation.

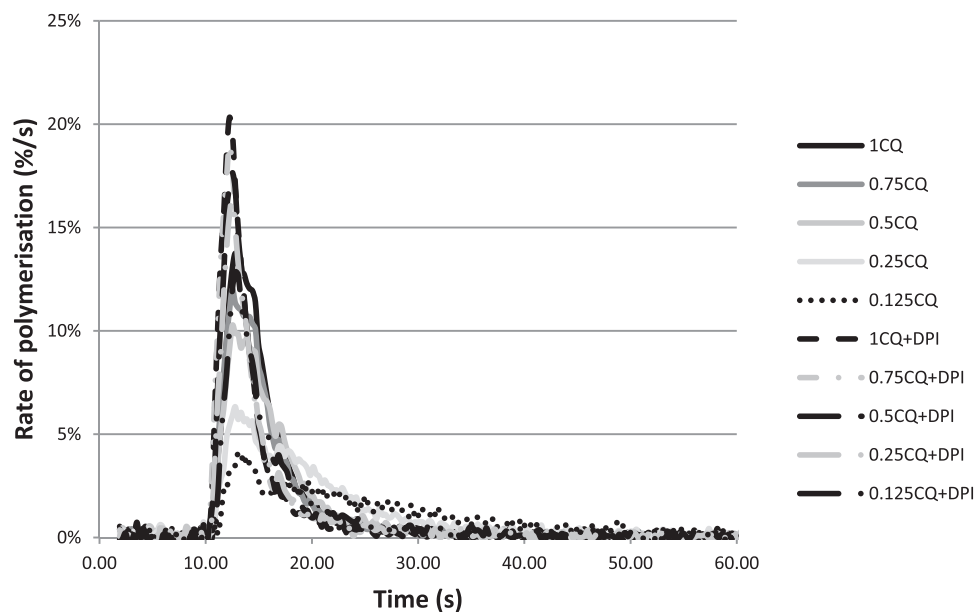


Fig. 3. Polymerisation rate (%/s; $n = 5$) as a function of time of the evaluated ERCs. The reduced rate of polymerization was apparent in the composites containing 0.125 and 0.25 CQ compared to the other groups. The first ten seconds were used as a baseline without irradiation.

compared with those without DPI at similar CQ concentrations, was observed (Table 2). Given the comparable degree of conversion achieved in both resin formulations (with and without DPI), this slight and potentially not clinically relevant reduction in light transmission (approximately 20 mW/cm²) could be attributed to an increase in resin opacity caused by the addition of DPI salt.

The superior DC observed in DPI-containing composites (excepting for CQ 0.5–1 mol%) compared with those lacking iodonium salt underscores the efficacy of DPI in facilitating a greater generation of free radicals for polymerization (3 instead of 1, as seen with the binary system) [1,14]. Also, DPI functions by minimizing the electron

back-transfer from the ketone radical anion and the amine radical cation. DPI intercepts the ketone radical anion, preventing electron back-transfer, and undergoes irreversible decomposition to an aryl radical and an aryl iodide [13,16]. Furthermore, the findings highlight the efficacy of combining DPI with very low concentrations of CQ, which promotes the production of resin composites with reduced CQ content, minimal yellowing and enhanced polymerization capacity.

The temperature during polymerization rose in accordance with the increase in the ERCs' polymerization rate, which varies depending on the reactivity of each material. Composites lacking DPI addition exhibited a smaller and slower temperature increase during

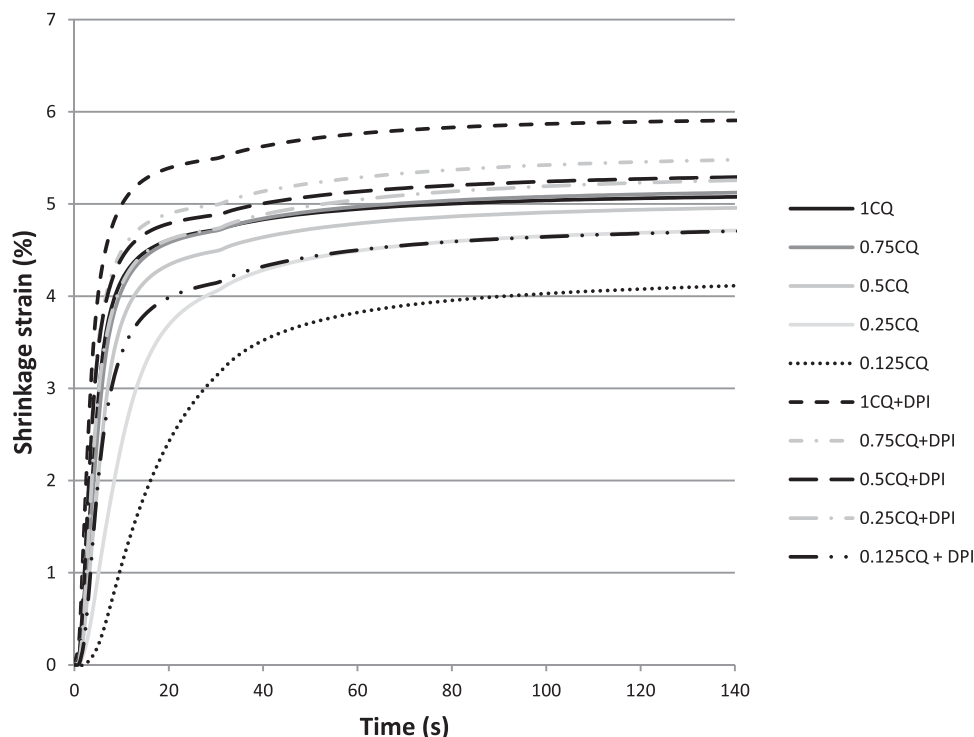


Fig. 4. Graphical representation of the real-time shrinkage of the evaluated ERCs (n = 3). The lower shrinkage strain presented by the composites containing 0.125 CQ is apparent, while the ERC with 1CQ+DPI demonstrated the highest shrinkage, with rapid development in the first seconds of curing.

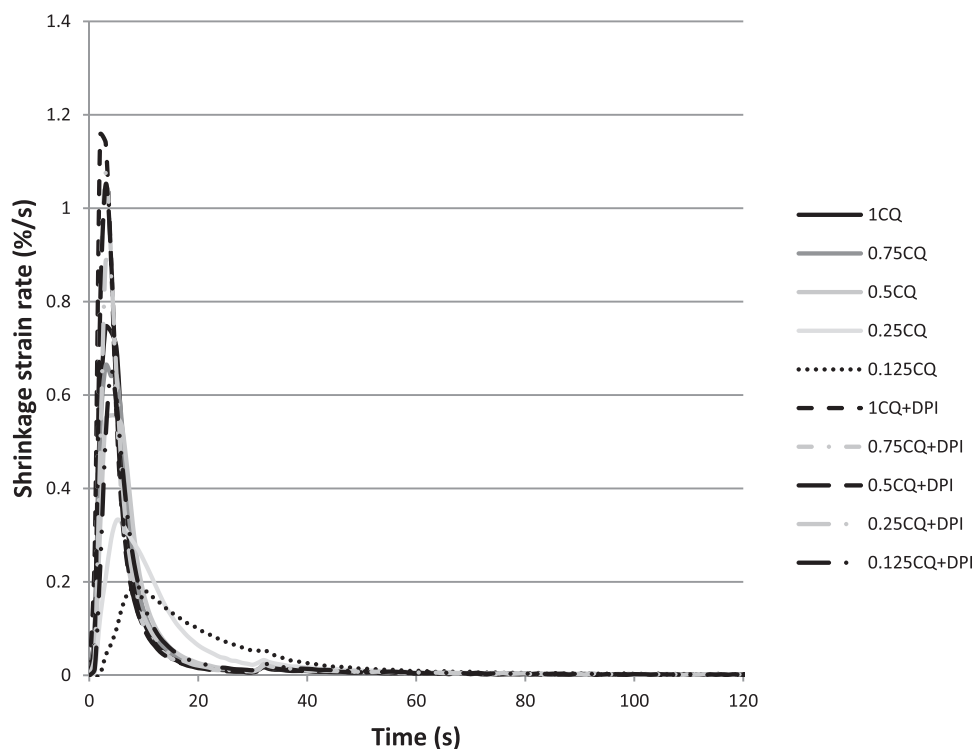


Fig. 5. Polymerisation shrinkage rate of ERCs evaluated according to CQ concentrations and presence of DPI (n = 3). The rate of shrinkage strain was similar to the rate of polymerisation, with the composites containing 0.125 and 0.25 CQ exhibiting the lowest shrinkage strain compared to the other groups.

polymerization. Given that free-radical polymerization reactions are inherently exothermic, the rapid and abundant formation of free radicals during the induction phase leads to a greater number of double bonds breaking (from C=C to C-C), thereby releasing energy in the form of heat [20].

In addition to the observed temperature increase, another characteristic noted with the addition of DPI was an increase in composite polymerization shrinkage. The heightened system reactivity, leading to a slight increase in DC (Degree of Conversion) and a significant increase in polymerization rate, likely induced changes in the formed polymeric

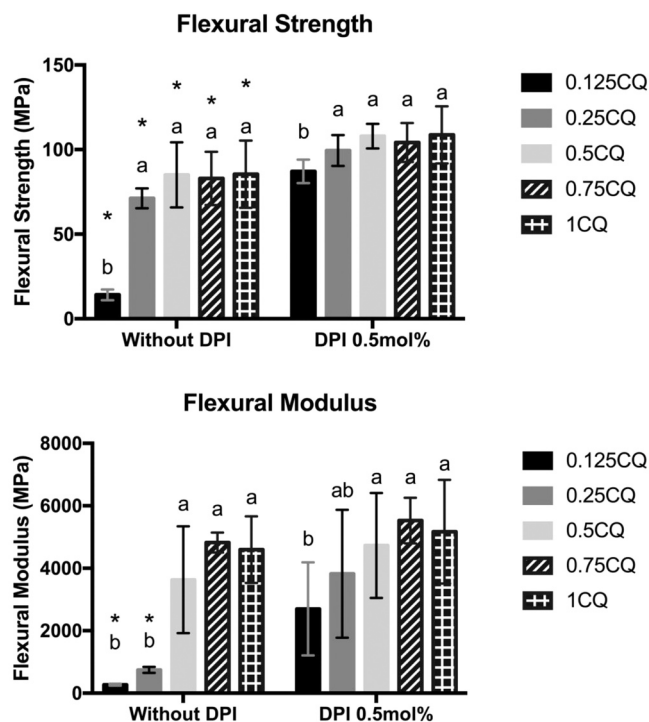


Fig. 6. Flexural strength and elastic moduli ($n = 12$) of the evaluated ERCs. Different letters indicate statistical differences. Lower case letters compare different amount of CQ. * indicates the statistical difference between groups without DPI to the DPI containing composites. ANOVA two-way and Tukey's test ($\alpha = 0.05$).

network, resulting in a notable rise in polymerization shrinkage. Previous studies have also demonstrated similar findings, showing increased polymerization shrinkage with the addition of DPI [10,14].

The utilization of DPI positively impacted properties such as water sorption, solubility, flexural strength, and modulus, particularly in composites with low concentrations of CQ. The enhancement in RP, DC, and potentially increased crosslinking density in DPI-containing composites are key factors contributing to this improvement, aligning with findings from previous research [2,3,10,12,21,22]. For low CQ concentrations, the incorporation of DPI led to a significant reduction in water sorption and composite solubility. However, for concentrations exceeding 0.5 mol% of CQ, the presence of DPI had limited effects, likely due to the equivalent conversion of high CQ concentrations regardless of the use of DPI. Moreover, the heightened radical production also entails an increase in radical-radical terminations and the number of growth centers, resulting in more shorter polymer chains and diminished crosslinking, directly influencing DC and polymer properties, thereby limiting or even reducing them.

A similar trend was observed for flexural modulus, particularly at low CQ concentrations (0.125 and 0.25 mol%). However, concerning flexural strength, the inclusion of DPI led to a noteworthy increase across all evaluated CQ concentrations. This aligns with prior studies where flexural strength was more affected by the use of iodonium salt compared to alterations in the elastic modulus of composites [3,10,22].

The present study presents promising findings regarding the utilization of very low concentrations of CQ (0.125 and 0.25 mol%) in conjunction with DPI for the preparation of restorative composites. These combinations yield properties akin to those observed in composites containing higher concentrations (0.75 and 1 mol%) of this initiator. Such results hold significance as they advocate for the use of reduced concentrations of CQ and tertiary amines in the initiator system, thereby promoting the production of less yellowish composites due to the reduced influence of CQ yellowing on the material. Moreover, it

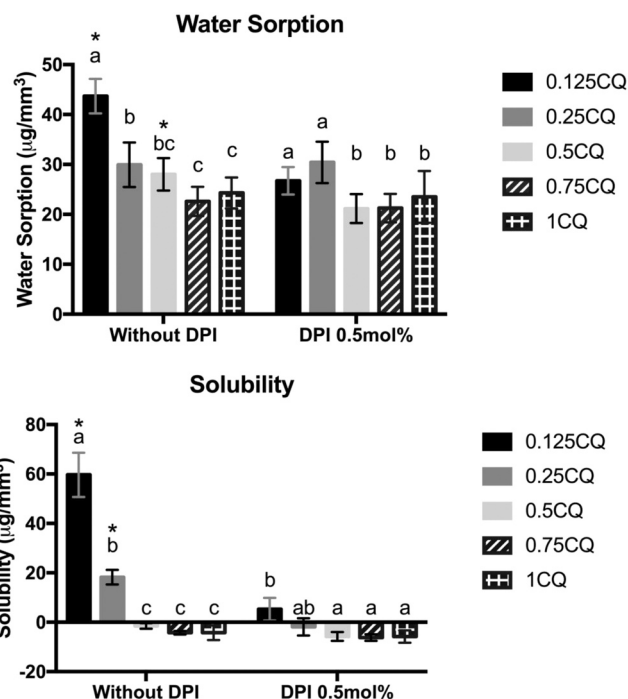


Fig. 7. Water sorption and solubility of composites according to CQ concentration and presence of DPI. Different letters indicate statistical differences. Lower case letters compare different amount of CQ. * indicates the statistical difference between groups without DPI to the DPI containing composites. ANOVA two-way and Tukey's test ($\alpha = 0.05$).

shows that CQ can be used efficiently in lower concentrations when associated with an iodonium salt, obtaining polymers with good physical properties, and cured with a widely-used blue band LCU.

5. Conclusions

The increased reactivity promoted by DPI can effectively offset the reduction in CQ/amine, resulting in enhanced physicochemical properties. However, it is essential to acknowledge that composites containing DPI also exhibit an increase in shrinkage rate and temperature during polymerization, which should be considered as potential drawbacks and carefully assessed in the development of ternary systems.

ERCs formulated with 0.25 mol% CQ - 0.5 mol% EDAB, and 0.5 % DPI demonstrated satisfactory performance in terms of degree of conversion (DC), maximum polymerization rate (RPmax), and mechanical properties, with a slight elevation in polymerization temperature and intermediate shrinkage strain.

Disclosure

Given his role as Editor in Chief, Dr David Watts had no involvement in the peer review of this article and has no access to information regarding its peer review. Full responsibility for the editorial process for this article was delegated to Dr Nick Silikas, Editor.

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. The authors would like to thank Esstech, Inc. (Essington, PA, USA) to partially provide the resin materials used in the present study.

References

- [1] Dressano D, Salvador MV, Oliveira MT, Marchi GM, Fronza BM, Hadis M, et al. Chemistry of novel and contemporary resin-based dental adhesives. *J Mech Behav Biomed Mater* 2020;110:103875.
- [2] Lima AF, Salvador MVO, Dressano D, Saraceni CHC, Goncalves LS, Hadis M, et al. Increased rates of photopolymerisation by ternary type II photoinitiator systems in dental resins. *J Mech Behav Biomed Mater* 2019;98:71–8.
- [3] Andrade KM, Paliolol AR, Lancellotti AC, Aguiar FH, Watts DC, Goncalves 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;32:749–55.
- [4] Guimaraes T, Schneider LF, Braga RR, Pfeifer CS. Mapping camphorquinone consumption, conversion and mechanical properties in methacrylates with systematically varied CQ/amine compositions. *Dent Mater* 2014;30:1274–9.
- [5] Hadis MA, Shortall AC, Palin WM. Specimen aspect ratio and light transmission in photoactive dental resins. *Dent Mater* 2012;28:1154–61.
- [6] Palin WM, Leprince JG, Hadis MA. Shining a light on high volume photocurable materials. *Dent Mater* 2018;34:695–710.
- [7] Randolph LD, Steinhaus J, Moginger B, Gallez B, Stansbury J, Palin WM, et al. Photopolymerization of highly filled dimethacrylate-based composites using Type I or Type II photoinitiators and varying co-monomer ratios. *Dent Mater* 2016;32:136–48.
- [8] Randolph LD, Palin WM, Watts DC, Genet M, Devaux J, Leloup G, et al. The effect of ultra-fast photopolymerisation of experimental composites on shrinkage stress, network formation and pulpal temperature rise. *Dent Mater* 2014;30:1280–9.
- [9] Sprick E, Becht JM, Graff B, Salomon JP, Tigges T, Weber C, et al. New hydrogen donors for amine-free photoinitiating systems in dental materials. *Dent Mater* 2021;37:382–90.
- [10] Verzola KC, Dressano D, Saraceni CHC, Goncalves LS, Hadis M, Watts DC, et al. Bis (4-methyl phenyl)iodonium as an alternative component to diphenyliodonium in camphorquinone-based ternary initiating systems. *Dent Mater* 2020;36:1282–8.
- [11] Min SH, Ferracane J, Lee IB. Effect of shrinkage strain, modulus, and instrument compliance on polymerization shrinkage stress of light-cured composites during the initial curing stage. *Dent Mater* 2010;26:1024–33.
- [12] Dressano D, Paliolol AR, Xavier TA, Braga RR, Oxman JD, Watts DC, et al. Effect of diphenyliodonium hexafluorophosphate on the physical and chemical properties of ethanolic solvated resins containing camphorquinone and 1-phenyl-1,2-propanedione sensitizers as initiators. *Dent Mater* 2016;32:756–64.
- [13] Oxman JD, Jacobs DW, Trom MC, Sipani V, Ficek B, Scranton AB. Evaluation of initiator systems for controlled and sequentially curable free-radical/cationic hybrid photopolymerizations. *J Polym Sci Pol Chem* 2005;43:1747–56.
- [14] Goncalves LS, Moraes RR, Ogliaeri FA, Boaro L, Braga RR, Consani S. Improved polymerization efficiency of methacrylate-based cements containing an iodonium salt. *Dent Mater* 2013;29:1251–5.
- [15] Lopes MB, dos Santos AMT, Coelho D, Gonini A, Ogliaeri FA, de Moraes RR. Influence of diphenyliodonium hexafluorophosphate on the bond strength and mechanical properties of model resin cements. *Int J Adhes Adhes* 2013;47:125–8.
- [16] Ogliaeri FA, Ely C, Petzhold CL, Demarco FF, Piva E. Onium salt improves the polymerization kinetics in an experimental dental adhesive resin. *J Dent* 2007;35(7):583.
- [17] Watts DC. Reaction kinetics and mechanics in photo-polymerised networks. *Dent Mater* 2005;21:27–35.
- [18] Hadis MA, Tomlins PH, Shortall AC, Palin WM. Dynamic monitoring of refractive index change through photoactive resins. *Dent Mater* 2010;26:1106–12.
- [19] Shortall AC, Palin WM, Burtscher P. Refractive index mismatch and monomer reactivity influence composite curing depth. *J Dent Res* 2008;87:84–8.
- [20] Schneider LF, Consani S, Sinhoretta MA, Sobrinho LC, Milan FM. Temperature change and hardness with different resin composites and photo-activation methods. *Oper Dent* 2005;30:516–21.
- [21] Salvador MV, Fronza BM, Pecorari VGA, Ogliaeri FA, Braga RR, Oxman JD, et al. Physicochemical properties of dental resins formulated with amine-free photoinitiation systems. *Dent Mater* 2021;37:1358–65.
- [22] Paliolol AR, Martins CP, Dressano D, Aguiar FHB, Goncalves LS, Marchi GM, et al. Improvement on properties of experimental resin cements containing an iodonium salt cured under challenging polymerization conditions. *Dent Mater* 2021;37:1569–75.