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Ultra-fast light-curing resin composite with increased conversion and reduced monomer elution

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ABSTRACT

Objectives. To test the null hypotheses that photoactive resin composites containing a Type I photoinitiator would exhibit reduced DC or increased monomer elution at substantially short curing times compared with materials based on a Type 2 ketone/amine system.

Methods. Two experimental resin composites were prepared, using either Lucirin-TPO or camphorquinone/DMAEMA. Specimens were light-cured using appropriate spectral emission that coincided with the absorption properties of each initiator using different irradiation protocols (0.5, 1, 3, 9 s at 500, 1000 and 2000 mW/cm^2 for Lucirin-TPO based composites and 20 or 40 s at 1000 mW/cm^2 for Lucirin-TPO and camphorquinone-based composites). Degree of conversion (DC) was measured by Raman spectroscopy, propagating radical concentrations were collected by means of electron paramagnetic resonance (EPR) and monomer leaching was characterized using high-performance liquid chromatography (HPLC).

Results. The null hypotheses were rejected, except for a single irradiation protocol (0.5 s @ 500 mW/cm^2). Lucirin-TPO-based composites could cure 20 times faster and release at least 4 times less monomers in comparison to camphorquinone-based composites. At 1000 mW/cm^2, and 1 s irradiation time for curing times of 1 s, Lucirin-TPO based composites displayed 10% higher DC. The difference in polymerization efficiency of Lucirin-TPO compared with camphorquinone-based resin composites were explained using EPR; the former showing a significantly greater yield of radicals which varied logarithmically with radiant exposure.

Significance. Lucirin-TPO is substantially more efficient at absorbing and converting photon energy when using a curing-light with an appropriate spectral emission and otherwise a limitation noted in several previous publications. At concentrations of 0.0134 mol/L,

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Lucirin-TPO-based composites require a minimum light intensity of 1000 mW/cm^2 and an exposure time of 1 s to provide significantly improved DC and minimal elution compared with a conventional photoinitiator system. The use of a wide range of curing protocols in the current experiment has realized the significant potential of Lucirin-TPO and its impact for clinical applications, in replacement to materials using camphorquinone.

1. Introduction

The degree of conversion (DC) of dental resin-based composites is a key physical property of the polymer since functional material characteristics, such as mechanical properties, volumetric shrinkage, wear resistance and monomer elution are significantly correlated [1]. Incomplete monomer conversion is a well-known drawback of dental resin composites, and the resulting monomer release [2] could at least partially account for failures observed clinically, including persistant post-operative sensitivity and/or the need for endodontic treatment, as well as secondary caries [3–6]. Further, the release of un-reacted monomers was suggested to be responsible for undesirable biological responses, such as cytotoxicity or disturbance of pulp progenitor cells differentiation even at non-toxic concentrations [7]. Therefore, incomplete polymer conversion and the increased potential for monomer release is likely to affect the delicate balance between healing and chronic inflammation in damaged pulp tissues [8,9]. Moreover, sub-optimal polymerization of resin composites may promote bacterial colonization at its surface [10]. It has also been suggested that release of degradation by-products from the monomers in dental resin composites can potentially influence biofilm formation and microbial survival at the material surface [11].

Clinically, the most common strategy to maximize DC and minimize monomer elution is to provide sufficient energy to the system by increasing curing time. Several works focusing on commercially available composites have emphasized the need to apply at least 20 s, but more likely 40 s irradiation to minimize the amount of eluted substances, even with the use of high irradiance LED lights [12–14]. As stated by Polydorou et al. [13], even 40 s irradiation "seems insufficient in order to prevent a high release of monomer". Currently, the general consensus in the clinics to light-cure a 2 mm layer of CQ-based commercial composites is 20 s at about 1000 mW/cm^2 with commercial LED polywave lights [15,16]. The industry is challenged to combine improvement of DC and decrease of monomer elution with a curing time as short as possible to satisfy the demands of a time-conscience dental practitioner. One interesting approach to significantly reduce curing time (3 s) while reaching similar or improved DC is to replace the conventional camphorquinone/amine system (CQ) (Type II initiator) with a Norrish Type I monoacylphosphine oxide photoinitiator, namely Lucirin-TPO (TPO) [17]. In a subsequent paper by the same group, it was reported the increased reaction speed did not lead to any increase in shrinkage stress, cusp deflection or marginal leakage, but significantly improved mechanical properties [18]. However, the impact of replacing a Type 2 with a Type 1 photoinitiator with regards to monomer elution has not been investigated to date.

Hence, the aim of the present study was to test the null hypotheses that at very short curing times, TPO-based resin composites would not exhibit any difference with regard to (1) DC or (2) monomer elution compared to a conventional CQ-based experimental composite.

2. Materials and methods

2.1. Materials

Two experimental resin composites were prepared, based on a 70/30 wt% Bis-GMA/TegDMA resin (Sigma Aldrich), using two different photoinitiator systems in equimolar concentrations (0.0134 mol/L): either camphorquinone and dimethylaminoethyl methacrylate 0.2/0.8 wt% (Sigma Aldrich), or Lucirin-TPO 0.42 wt% (BASF), subsequently referred as CQ and TPO, respectively. CQ concentrations were chosen in order to be within the region of maximum DC according to Yoshida and Greener [19]. The corresponding equimolar concentration of TPO also falls within the range described as adequate with regards to DC, since Miletic and Santini reported that any concentration in excess of 0.43 wt% resulted in only very small increase in DC values [20]. Hence, the concentration of both photoinitiators can be considered to be in the optimal range, which enables the comparison of both initiating systems in optimal conditions.

The following fillers were introduced to the resin matrix: silanated barium glass (G018-186/K6, $d_{50} = 3 \pm 1\,\mu$m, Schott AG, Germany) and methacrylsilane treated fumed silica (12 nm, Evonik Industries, Germany) at 65 and 10 wt%, respectively. This is summarized in Table 1.

2.2. Light curing

Specimens were polymerized in Teflon moulds of 2 mm thickness and 5 mm diameter, covered on each side by Mylar films, resting on a glass slide. For the EPR measurements, rectangular specimens of dimensions 5 × 2 × 2 mm were prepared, also in Teflon moulds. Light-curing was carried out with an AURA light device (Lumencor, USA) providing narrow spectral outputs. Irradiation could be applied independently at two wavelength ranges: 395–415 nm and 455–485 nm for TPO and CQ-based composites, respectively as shown in Fig. 1. Light irradiance calibrations were carried out directly at the tip of the optic fiber light guide (6 mm diameter) with good linear fit ($R^2 > 0.98$), using a calibrated and NIST traceable deuterium tungsten light source (DH2000-CAL, Ocean Optics, Dunedin, USA). Calibration and spectral irradiance

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Table 1 – Experimental composites formulations.

Composite	Monomers (ratio)	Photoinitiators	Fillers
CQ	Bis-GMA: 70 wt% TegDMA: 30 wt%	Camphorquinone: 0.2 wt%[a] 2-(Dimethylamino)ethyl methacrylate: 0.8 wt%[a]	Micro/nano (65/10 wt%)[b]
TPO	Bis-GMA: 70 wt% TegDMA: 30 wt%	Lucirin: 0.42 wt%[a]	Micro/nano (65/10 wt%)

Bis-GMA—bisphenol A glycol dimethacrylate
TegDMA—triethyleneglycol dimethacrylate
Micro—silanated barium glass Ø 3 μm
Nano—methacrylsilane treated fumed silica Ø 12 nm

[a] Percentage of monomer content only.
[b] Percentage of total composite mass, including monomer and photoinitiator.

Table 2 – Description of curing protocols applied for CQ- and L-based specimens.

Composite type	I_{irr} (mW/cm^2)	t_{irr} (s)
CQ	1000	40 and 20
TPO	2000 (H_{irr})	9, 3, 1 and 0.5
	1000 (M_{irr})	40, 20, 9, 3, 1 and 0.5
	500 (L_{irr})	9, 3, 1 and 0.5

measurements were performed using a spectrophotometer (USB4000, Ocean Optics) with an 8 μm diameter fiber connected to a 3.9 mm opaline glass cosine corrector aligned concentrically with the light guide of the curing light device. Light irradiance in each range could be varied from 60 to 3240 mW/cm^2 and 30 to 1360 mW/cm^2, for TPO and CQ-based resin composites, respectively. Light curing was carried out with the light guide tip in direct contact with the upper Mylar film. As mentioned above, while 20 s are recommended in clinical practice, it is safer in terms of monomer elution to use 40 s for CQ-based materials. For these reasons, controls in the present work were experimental CQ-based composites light-cured at 1000 mW/cm^2 for 20 and 40 s. However, TPO-based experimental composites may require much shorter irradiation times and were cured at 2000 mW/cm^2 for 9 s, 3 s, 1 s or 0.5 s, 1000 mW/cm^2 for 40 s, 20 s, 9 s, 3 s, 1 s or 0.5 s and 500 mW/cm^2 for 9 s, 3 s, 1 s or 0.5 s. This is summarized in Table 2. Irradiation time was adjusted using an automatic sequence mode available in the controlling software which allowed for flashes as short as 0.2 s with precise execution.

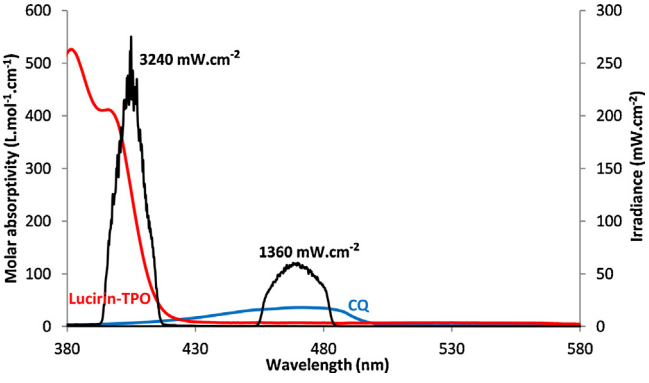

Fig. 1 – Spectral output at maximum irradiance of the AURA light engine and absorption profile of CQ and TPO photoinitiators.

Radiant energy (J/cm^2), defined as the product of irradiance (W/cm^2) and irradiation time (s) ranged from 0.25 to 40 J/cm^2 and 20 to 40 J/cm^2 for TPO and CQ-based composites, respectively (Table 3).

2.3. *Degree of conversion*

DC was measured by Raman spectroscopy, carrying out three measurements for each sample surface (upper and lower), at least 20 min following irradiation ($n = 3$). The equipment used was a Raman Spectrometer (DXR Raman Microscope, Thermo Scientific, Madison, WI, USA), with a 1 μm spatial resolution and 3 cm^{-1} spectral resolution. The samples were excited at 780 nm by a frequency-stabilized single mode diode laser through a microscope objective (×50) with the following conditions: microhole, 50 μm; irradiation time, 60 s; number of accumulations, 5; grating 400 lines/mm. The DC was then calculated as the percentage of vinyl functions converted to aliphatic functions based on the decrease in the C=C bond peak at 1640 cm^{-1} compared to the uncured sample; the aromatic C=C peak at 1610 cm^{-1} was used as the internal standard.

2.4. *Free radical concentration*

Post-curing signals from trapped free radicals were analyzed using a MINISCOPE MS200 EPR spectrometer (Magnettech, Germany), equipped with a rectangular cavity (TE102) with parameters previously described [21–23]. Briefly, the height of the fourth peak (from 336.1 to 336.6 mT of the magnetic field, g-factor 2.02) was measured after 5 min, 1 h, 24 h, 1 week and 1 month after irradiation ($n = 3$) to determine the relative concentration of trapped propagating radicals.

2.5. *Monomer elution*

Immediately after light curing, specimens were weighed and placed in 10 mL of 75/25 vol% ethanol/water solution. Elution medium was prepared using absolute ethanol NORMAPUR® (purity 99.8%, CAS: 64-17-5, VWR) and Milli-Q® water (Millipore, Merck). 1 mL eluates were taken for HPLC analysis at 1 h, 6 h, 24 h, 72 h and 1 week ($n = 3$), each removed volume being immediately replaced by an equivalent amount of fresh ethanol/water solution. Specimens were stored in the dark at 37 °C between measurements.

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Table 3 – Elution of monomers after one week and degree of conversion (UP is the upper surface): means (s.d.).

	Curing time (s)/irradiance (mW/cm^2)	Radiant exposure (J/cm^2)	Bis-GMA (wt/wt%)	TegDMA (wt/wt%)	DC (%)
TPO	0.5/500	0.25	25.5^A	18.4^D	51 (3) UPPER
			(2.2)	(1.9)	38 (6) LOWER
	1/500	0.5	8.2^B	4.5^E	57 (2) UPER
			(0.9)	(0.4)	51 (2) LOWER
	3/500	1.5	2.4^C (0.4)	0.4^F (0.1)	59 (4)
	9/500	4.5	1.6^C (0.1)	b.l	60 (4)
	0.5/1000	0.5	9.1^B (1.8)	5.1^E (1.1)	62 (0.4) UPPER
					55 (2) LOWER
	1/1000	1	2.9^C (0.9)	0.7^F (0.3)	64 (4)
	3/1000	3	1.3^C (0.3)	b.l	64 (2)
	9/1000	9	1.3^C (0.3)	b.l	62 (3)
	20/1000	20	1.2^C (0.2)	b.l	62 (3)
	40/1000	40	1.3^C (0.2)	b.l	63 (2)
	0.5/2000	1	2.7^C (0.4)	0.8^F (0.3)	57 (5)
	1/2000	2	1.4^C (0.1)	b.l	59 (2)
	3/2000	6	1.2^C (0.2)	b.l	60 (4)
	9/2000	18	1.2^C (0.3)	b.l	58 (4)
CQ	20/1000	20	7.2^B (1.9)	3.6^E (1.1)	51 (3)
	40/1000	40	6.8^B (1.3)	3.2^E (0.7)	51 (3)

Means with same superscript symbol do not differ significantly ($p < 0.01$).
b.l, below quantification limit. DC values indicated were calculated as the means for upper and lower surfaces rounded up. When DC values for upper and lower surfaces presented a significant difference ($p > 0.05$), according values were specified.

Analysis by reverse phase HPLC was carried out on a Hitachi D-7000 module equipped with a Waters Symmetry C18 3.5 μm column of dimensions 4.6 × 75 mm, along with a Hitachi L-7455 Diode Array Detector. Analysis was carried out at 210 nm for both monomers. Solvents used were water (H_2O, A) and acetonitrile (ACN, B) of HPLC grade. Mixtures of A and B were applied as follows: gradient mode, flow rate of 1.2 mL/min, starting at 100:0 (A:B), maintained for 1 min, then decreased to reach 0:100 in 6 min, then maintained for 1 min.

Calibration curves were determined for both monomers introduced in the composites (Bis-GMA, and TegDMA) by measuring absorption peak areas at different concentrations (from 10^{-2} to 10^4 μg/mL). Bis-GMA produced several noticeable peaks. Commercial monomers contain a variety of isomers and by-products from synthesis and hence may release different components (Y. Imai, 2000). For quantification of Bis-GMA, the most intense peak noted was selected since the supplier indicated a 92% purity level. In both calibrations, the goodness of fit was excellent ($R^2 = 0.998$ and 0.999 for Bis-GMA and TegDMA, respectively). The entire specimen surfaces were considered to be exposed to the elution fluid (0.12 cm^2). Following the recommendations of Van Landuyt et al. [24], amounts leached were expressed in terms of relative amounts of their initial content (wt/wt, in %). Quantities released were referred to as $Q_{Bis\text{-}GMA}$ and Q_{TegDMA}.

2.6. *Statistical analysis*

The JMP 8 software was used for all statistical analyses. These were performed on DC (individual and average: mean of DC of upper and lower surfaces), propagating radical concentration, $Q_{Bis\text{-}GMA}$ and Q_{TegDMA}, using one-way analysis of variance (ANOVA) and Tukey's test for multiple comparisons. The interactions between DC, photoinitiator type, irradiation parameters, radiant energy and time intervals (when appropriate) were studied by multivariate analysis (pairwise comparison). Sets of variables were transformed to obtain normal distributions.

3. Results

For all properties, no statistical difference was observed between CQ-based materials cured during 20 or 40 s ($p > 0.05$). Hence, they will not be discriminated in the rest of the work, and be referred to as CQ-based controls.

For CQ-based controls, similar DC were observed for upper and lower surfaces (50 ± 2% and 52 ± 1% for upper and lower surfaces, respectively), or an average of 51 ± 3% (Fig. 2). For TPO-based composites, DC reached similar values between upper and lower surfaces for each specific protocol, except for three conditions: 0.5 s at 1000 mW/cm^2, and 0.5 and 1 s at 500 mW/cm^2. For these parameters, a significant drop in conversion between lower and upper surfaces was noted ($p < 0.01$), in particular for 0.5 s at 500 mW/cm^2 with a 13% difference. Apart from these three exceptions, DC for TPO-based materials ranged from 57% to 64%, with an average of 59 ± 1%. Considering identical irradiation protocols as the controls (i.e. 1000 mW/cm^2, 20 or 40 s), DC for TPO-based composites was 63 ± 3%, i.e. 12% greater compared with that of CQ-composites. When comparing average DCs of upper and lower surfaces, CQ-composites were similar to TPO-composites cured at 500 mW/cm^2 for 1 s and 1000 mW/cm^2 for 0.5 s ($p > 0.05$) and significantly higher than 0.5 s at 500 mW/cm^2 ($p < 0.05$). A logarithmic fitting of average DCs versus radiant energy for TPO-composites presented a low correlation ($R^2 = 0.35$).

EPR measurements revealed the presence of trapped free radicals over a period of at least one month after light-curing. The rate of decay was similar for all composites and decreased logarithmically over time, with a change in slope after 24 h (Fig. 3a), in log × scale). The concentration of propagating

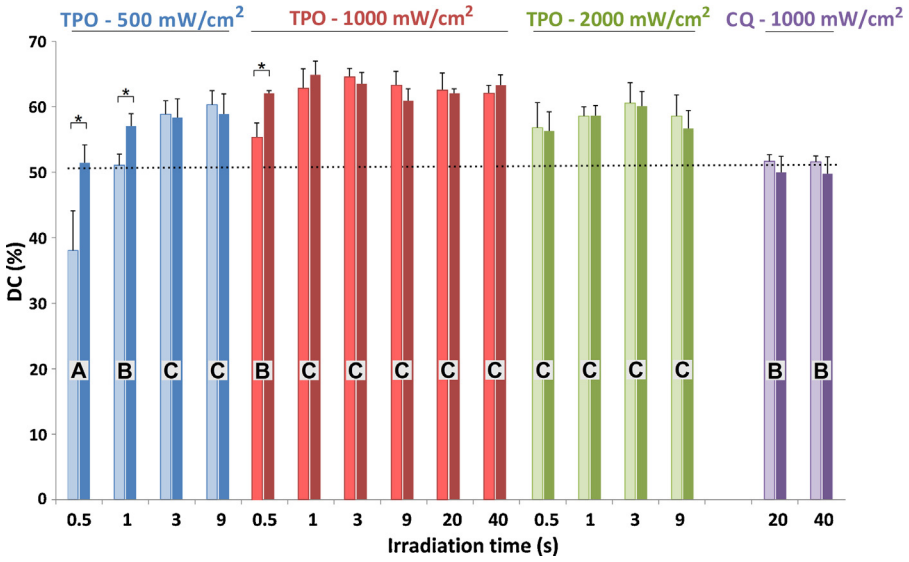

Fig. 2 – Degree of conversion (mean and standard deviations, in %, $n = 3$) for TPO and CQ-composites at various irradiation times (s) for TPO-composites irradiated at 500 and 2000 mW/cm^2 and TPO and CQ-composites irradiated at 1000 mW/cm^2. Histograms with light and dark shades correspond to lower and upper sample surfaces, respectively, * indicating statistically significant differences between both surfaces ($p < 0.05$).

radicals of TPO-based materials was 3 to 4 times larger than the CQ controls, except for the same three exceptions mentioned above relating to DC measurements, i.e. 500 mW/cm^2 for 1 s and 1000 mW/cm^2 or 500 mW/cm^2 for 0.5 s (about 2 times higher; $p < 0.05$ or comparable to the controls; $p > 0.05$, respectively) (as seen on Fig. 3b), 1 h after light-curing). Plotting EPR signal against radiant energy revealed that CQ had a significantly lower free radical yield compared with TPO (Fig. 4, in log × scale). In TPO-based materials, the propagating radical signal increased with radiant energy in a common manner for all three irradiances, and reached a plateau around 2–3 J/cm^2 (Fig. 4). A logarithmic fit between radical concentration and radiant energy gave higher correlation compared with that of DC measurements ($R^2 = 0.66$).

Release profiles of Bis-GMA and TegDMA over time for both composites are presented in Fig. 5a and b. All curves presented a good logarithmic fit and significant correlation between cumulative release and time ($R^2 > 0.9$). For all groups and curing modes, relative amounts of TegDMA were lower than those of Bis-GMA. Statistically, three separate groups for both monomers could be distinguished based on cumulative amounts leached after one week (Fig. 6a and b), $p < 0.01$). TPO-composite cured at 500 mW/cm^2 for 0.5 s exhibited 25.5 wt/wt% and 18.4 wt/wt% release of Bis-GMA and TegDMA after one week, respectively. CQ-controls along with TPO-composites cured at 500 mW/cm^2 for 1 s or at 1000 mW/cm^2 for 0.5 s exhibited a release between 9.1–8.2 wt/wt% and 5.1–4.5 wt/wt% for Bis-GMA and TegDMA, respectively. For the remaining curing conditions, TPO-composites released significantly less (maximum release of 2.9 wt/wt% and 0.8 wt/wt%) compared with CQ-controls and TPO-based materials cured at lower irradiance and/or short curing time. The lowest cumulative amounts released after one week for TPO-composites were 1 wt/wt% (13 μg/mL) for Bis-GMA whereas TegDMA levels dropped below the quantification limit (0.11 μg/mL). A significant negative correlation was found between DC and $Q_{Bis\text{-}GMA}$ (Pearson correlation coefficient = −0.86) and Q_{TegDMA} (−0.94) for TPO-composites.

4. Discussion

Both null hypotheses could be rejected since significant differences were observed for both DC and monomer elution. Apart from a single curing protocol (0.5 s @ 500 mW/cm^2), even at very short curing times (0.5 and 1 s) at higher irradiance, TPO-based resin composites exhibited similar or increased DC, and similar or reduced monomer elution compared with the conventional CQ-based experimental composites used as controls.

For TPO-based composites, the increased DC compared with CQ (Fig. 2) is in accordance with previous research using commercial halogen [17,25] or so-called “polywave” (multiple diode) LED lights [26,27]. In the present work, and to our knowledge, for the first time a specific light-curing device was used that provided three major advantages: (i) the selection of the emission wavelength range specific to each photoinitiator absorption spectrum compared with either broad-spectrum or multiple-diode LED curing lights (reducing unnecessary spectral mismatch that may be inefficient in terms of polymerization but may otherwise result in undesirable pulpal temperature rise [16]); (ii) modulation of the light output specifically and independently for each photoinitiator (Fig. 1); (iii) clinically relevant irradiance levels. Using this device, the irradiation times were shorter than described previously (3 s, [17]), without any DC reduction compared with the optimal DC, (except for 3 irradiation modes: 0.5 s at 500 mW/cm^2, 0.5 and 1 s at 1000 mW/cm^2). Hence, besides confirming the advantage of using TPO regarding DC for a 70/30 wt/wt% Bis-GMA/TegDMA filled composite, the present work provides the irradiation

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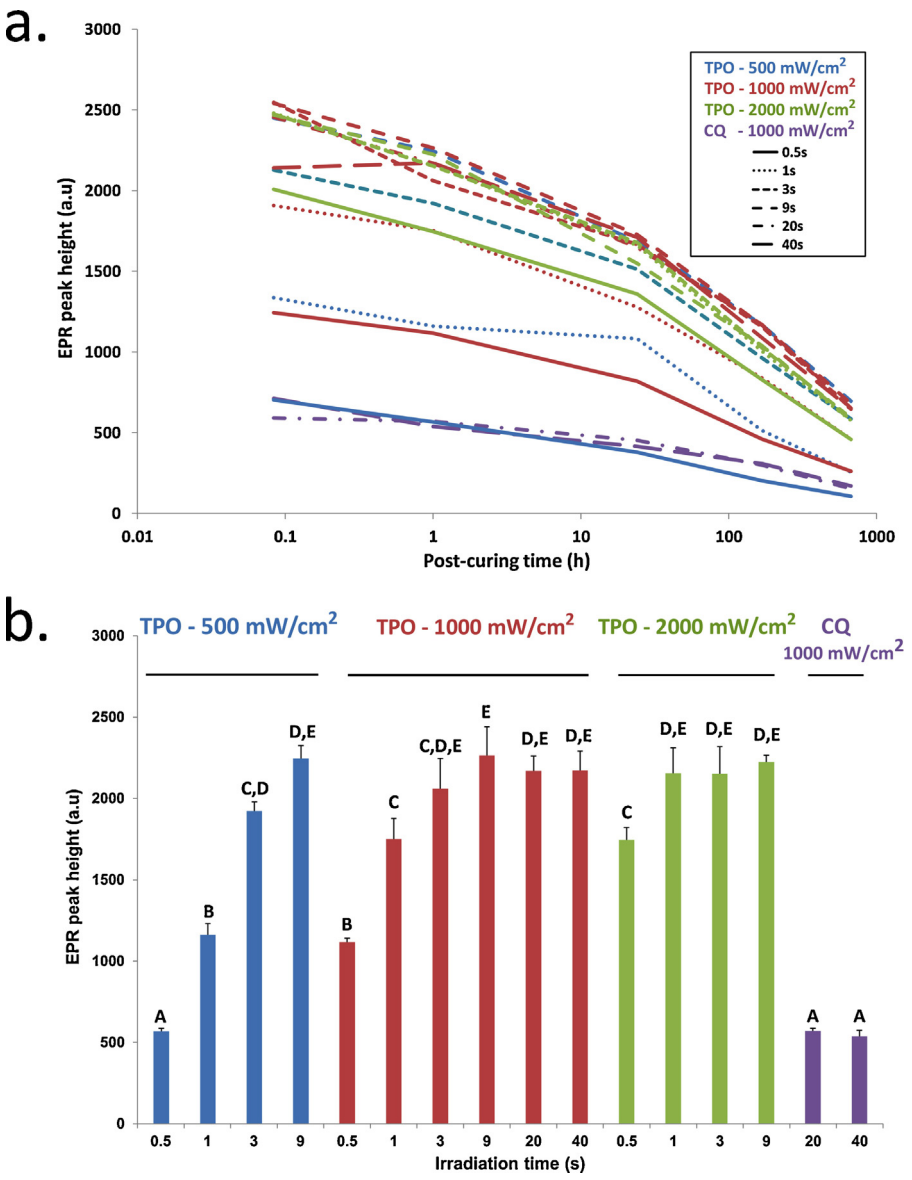

Fig. 3 – (a) EPR peak height (a.u.) from propagating radicals as a function of time (h) for both composite type and all curing protocols. Color indicate irradiance (mW/cm^2) and line design indicate irradiation time (s) and (b) EPR peak height (a.u.) at 1 h post-cure plotted against irradiation time (s) for both TPO and CQ-composites and grouped by irradiances (mW/cm^2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

parameters to reach optimal polymerization, as well as those that do not allow sufficient cure. The three exceptions exhibit a significant difference in DC between upper and lower surfaces, which may suggest an insufficient depth of cure. Lower depths of cure have previously been reported for TPO-based composites, though more than the 2 mm thickness limit and based on the ISO4049 or penetrometer methods [17,25].

The higher DC at lower curing times results from increased rates of polymerization enabled by TPO-compared with CQ-based composites [17] and can be explained by the substantially higher molar absorptivity (photon absorption ability) for TPO-compared with CQ over a significant portion of the absorbance/emission overlap, as illustrated by Fig. 1 and in line with previous work [28]. Also, the Lucirin-TPO molecule is able to cleave into two active radicals, which results in a greater quantum yield efficiency (a greater ability to produce active radicals from a given amount of photons), whereas CQ activation yields only one active radical per molecule through proton transfer. The difference in quantum yield efficiency between TPO and CQ was observed previously [29]. To better understand the differences in reactivity and polymerization efficiency between both photoinitiation systems, DC and elution measurements were complemented by EPR analyses. The latter was proven useful to better understand the impact on polymerization of clinically relevant irradiation parameters [23]. The increased ability of TPO to produce active radicals was confirmed by the EPR data, with a 3 to 4-fold higher radical concentration observed for most TPO-based composites (Fig. 3). In line with previous works, trapped free radicals were detected over several weeks [22] with a change of slope

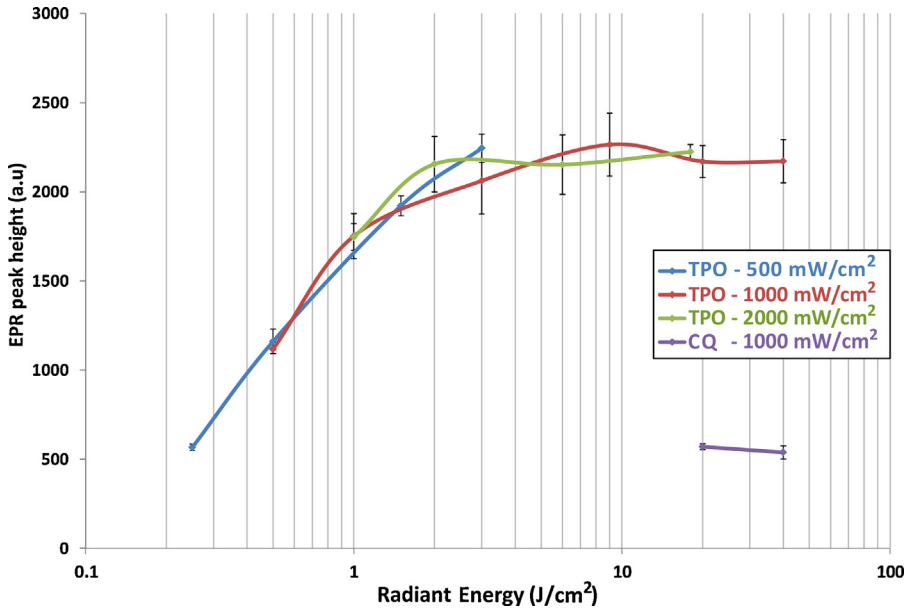

Fig. 4 – EPR peak height (a.u.) plotted against radiant energy (J/cm^2). Color indicates composite type and irradiance (mW/cm^2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the radical decay around 1 day post-cure [23] (Fig. 3a). In line with DC data, EPR measurements underlined the irradiation conditions leading to sub-optimal generation of free radicals (Fig. 3b). Given the strong relationship established between autoacceleration and radical entrapment [30], it is likely that autoacceleration in TPO-composites is of higher magnitude, with an early onset of gelation and possibly a delayed vitrification. The transition from optimal to sub-optimal curing conditions determined by radical entrapment (Fig. 3) corresponded to a change in polymerization kinetics closer to a CQ-like mechanism (smaller reaction rates and earlier onset of vitrification) and/or to a limited penetration of light in filled composite. However, both hypotheses cannot be discriminated using the current results since the EPR technique was a bulk measurement. The saturation of the EPR peak height seemed to correspond to an irradiation protocol where radiant energy was between 2 and 3 J/cm^2 (Fig. 4). Below this threshold, radical yield decreased (indicated by the amount of trapped radicals after curing). Hence, the present data enabled the identification of an optimal curing protocol, TPO-composites benefiting from high irradiances up to a point. Based on the criteria that upper and lower surfaces should display similar DC as an indicator of optimal curing, the optimal curing parameter for TPO-based composites is 1 s at 1000 mW/cm^2 for 2 mm thick layers. The improved overlap between light emission spectra and photoinitiator absorption spectra increased polymerization efficiency compared with previous work [28,29] resulting in an effective cure at very short curing times. Importantly, it does not seem necessary to increase either irradiance or irradiation time above the optimal values as physical material properties are unaffected.

Monomer release over the one-week period (Fig. 5) exhibited a logarithmic-like profile with most of the leaching occurring in the first 6 h. This was similar to what is usually observed, both in commercial and experimental resins and resin composites [31–33]. It has been proposed that two chronological events occur: first, increased elution rates (in the first 6 h) associated with less restricted release of un-reacted monomers from the surface, and second, a slower release rate of monomer leachates from the bulk [33]. This would imply a heterogeneous sample with a less converted surface compared to the bulk, which in the present work is the case for the three conditions with significant differences between upper and lower surface DC (0.5 s at 1000 mW/cm^2, and 0.5 and 1 s at 500 mW/cm^2). However, for all the other conditions, upper and lower surfaces display a similar DC, and a different release process between the bulk and the surface is then less likely. In this case, we suggest another explanation. It was described that solvents diffuse rapidly through the matrix, which is solely mediated by the extent of cross-linking and polar interactions with monomers [34]. It is also known that after polymerization, gel and fully vitrified domains co-exist in composite materials [35]. Hence we suggest that the initial quick release (<6 h) is due to the leaching from the gel domains and the leaching from the vitrified domains participate in the process on a much longer time scale (over a week in our case). Long-term release would then depend on crosslinking density hence on monomer type and ratio. As a result, longer release kinetics can sometimes be expected. For example, monomer release was observed in one study over a 3-week storage period [36].

Using Lucirin-TPO and an appropriate curing unit led to higher conversion degrees which may be associated with denser networks and reduced rates of release of Bis-GMA and TegDMA in comparison to systems using CQ. The results of monomer elution highlighted the same trends as for DC and free radical concentrations that led to sub-optimal polymerization of TPO-based composites using short exposure times

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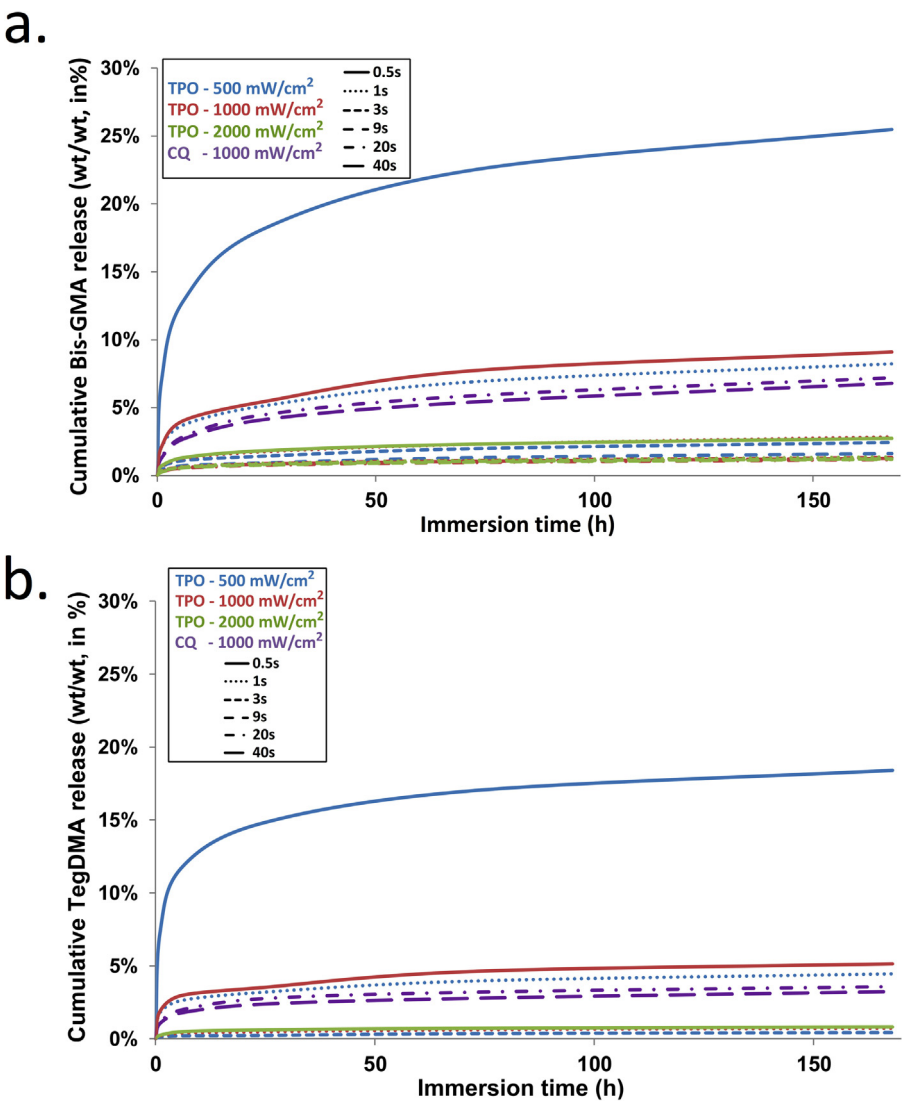

Fig. 5 – Cumulative release profiles of Bis-GMA (a) and TegDMA (b) (wt/wt%) over a one week storage period. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and lower irradiance, (0.5 s at 500 mW/cm^2, 1 s at 500 mW/cm^2 and 0.5 s at 1000 mW/cm^2). The gradient of polymerization within the sample can partially account for increased elution compared with other TPO-based samples and with slower polymerization kinetics (more similar to the reaction mechanism of CQ-based materials) free radical concentration is reduced (Fig. 3b). The very large and sudden monomer release for TPO-based resin composites cured at 500 mW/cm^2 for 0.5 s (almost 3× the eluate mass produced following a 1 s cure at the same irradiance) support the need for longer irradiation times if lower irradiances are used.

The strong inverse correlation of monomer release with DC described in the literature [2,12] was verified for TPO-based composites and outlined the importance of selecting an optimal irradiation protocol. At 1000 mW/cm^2 and 1 s, the TPO-composite released a total of 2.9 wt/wt% (37.4 μg/mL) of Bis-GMA and 0.7 wt/wt% (4.1 μg/mL) of TegDMA. These values correspond to similar or reduced amounts of eluted monomers compared to values reported in the literature for commercial composites using CQ but with much shorter curing times. In the work by Manojlovic et al. [33], where specimens of identical dimensions and similar elution protocol were used, Filtek Supreme cured for 20 s with a second generation LED Bluephase at 700 mW/cm^2 presented a released concentration of Bis-GMA of 42 μg/mL. Tetric Evo Ceram which was shown to contain both CQ and TPO [16,37] presented released concentrations of Bis-GMA of 101.6 μg/mL and of TegDMA of 36.6 μg/mL (where large amounts eluted in the first 24 h were excluded) when cured with a halogen light unit at 800 mW/cm^2 for 20 s. Manojlovic et al. [33] also investigated Tetric Ceram and found similar levels with a worsening of eluted levels when using Bluephase compared to a halogen. This is due to the use of a second generation LED unit (Single diode), which is inefficient below 430 nm, where TPO is active. The halogen light provides a broader irradiation spectrum, which overlaps the absorption spectrum of both CQ and TPO, as would third generation LED ("polywaves") units [38]. In comparison to the levels noted, average levels in our CQ-based

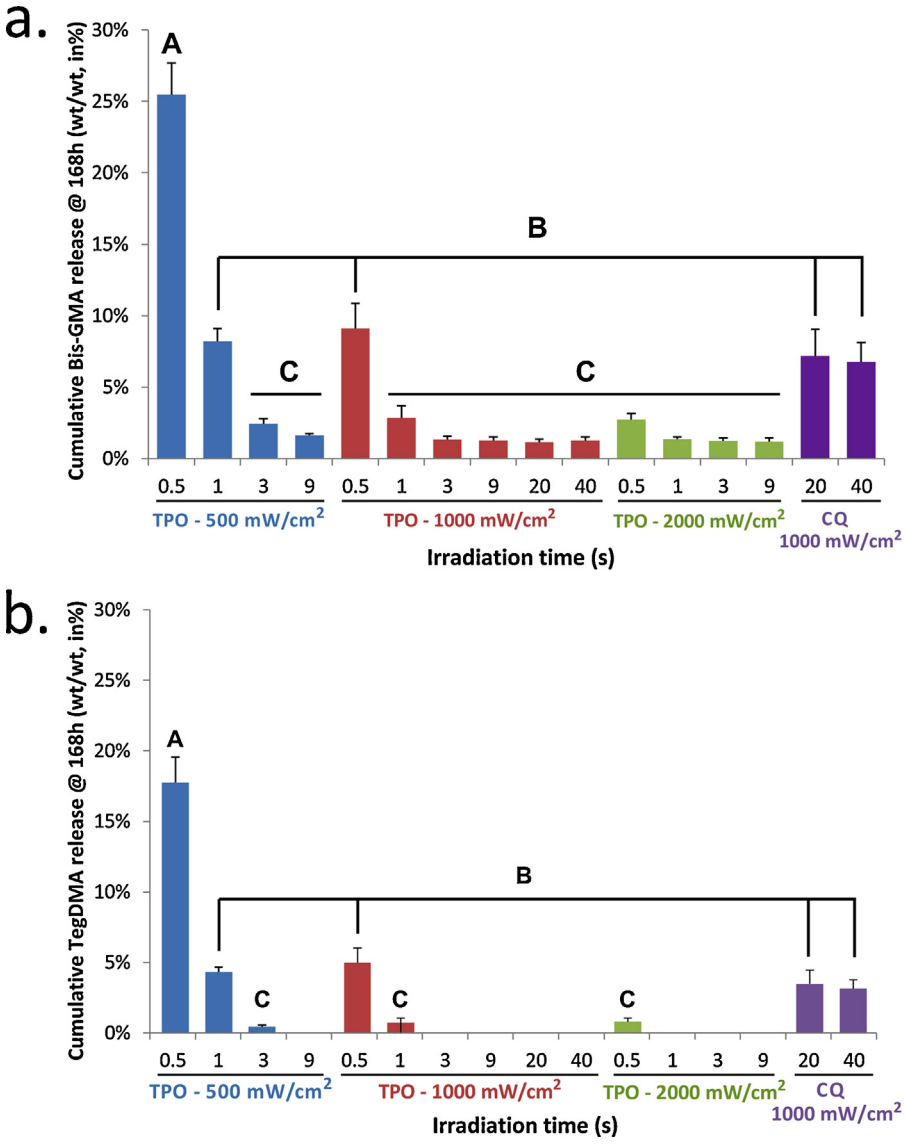

Fig. 6 – Amounts of Bis-GMA (a) and TegDMA (b) released after one week (means and standard deviations, $n = 3$) for TPO and CQ-composites. Values connected with similar symbol are statistically similar ($p > 0.05$).

resin composites were 105 μg/mL for Bis-GMA and 16 μg/mL for TegDMA. Commercial composites show a reduction of Bis-GMA and TegDMA release with increased curing time (up to 60 s) [12,31], although amounts of released monomers are comparable to our controls. It should be noted that in comparison to the latter, monomer elution was reduced at least 3-fold with the TPO-composites (except for the three sub-optimal curing conditions mentioned above). As already mentioned, this significant improvement is partly due to the use of a better adapted light-curing device, which underlines the possible need to adjust the commercial LED light-curing units currently available, notably by optimizing their spectrum to the new photoinitiator, and possibly by increasing their irradiance below 430 nm.

In accordance with previous work, the relative release (wt/wt, in %) of TegDMA was lower than the one of Bis-GMA [31]. This may be due to better conversion during polymerization, specifically with regards to the TegDMA molecule. TegDMA (M = 286 g/mol) being inherently more mobile than the more bulky Bis-GMA (M = 512 g/mol), it can be assumed that the former better diffuses during the gel-phase. This results in higher DCs in polymer mixtures with more TegDMA [39]. The leaching levels observed in the present study may be low enough to have little to no impact on dental tissues, which is currently under investigation by the authors. No toxic effects have been observed below 100 μg/mL for TegDMA [40] with, however, modified cell expression with respects to mineralization at 75 μg/mL [41]. No information regarding the effects of TPO-based resin composites on cellular behavior is currently available. In order to determine if TPO-based materials display improved biological compatibility, the biological material characteristics will also be investigated with similar irradiation parameters in future work.

Finally, besides intrinsic differences in polymerization efficiency due to increased radical production, any increase in reaction temperature may account for higher conversion by

delaying vitrification and increasing the glass transition temperature. These aspects are currently under investigation, and will be the topic of a subsequent paper. However, the data acquired at this point reveal that the maximum temperature reached during the polymerization of TPO-based composites is either lower or comparable to the CQ-based controls (20 and 40 s). Therefore, differences in reaction temperature do not seem to explain the differences in DC, elution and radical concentrations observed in the present work.

In summary, based on the data collected, the use of elution studies as an appropriate method to identify sub-optimal polymerization parameters is supported and possibly with more precision than the measurement of DC. As highlighted by the present data, the combined use of EPR, Raman and HPLC is certainly more powerful than isolated methods.

5. Conclusion

Experimental resin composites based on the Type 1 photoinitiator, Lucirin-TPO exhibited increased monomer conversion in comparison with conventional CQ-based materials, which in turn resulted in at least 3-fold reduction in monomer elution, both factors being strongly correlated. Using a light source with a spectral output specific to the absorption of the photoinitiator, it was possible to develop a material capable of achieving superior properties using an exposure time as short as 0.5 to 1 s for 2 mm-thick layers. From the results of the current study, replacement of a conventional Type 2 ketone/amine with a shorter wavelength, higher absorptivity Type 1 photoinitiatior in commercial products is supported.

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