Reduced polymerization stress of MAPO-containing resin composites with increased curing speed, degree of conversion and mechanical properties

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\textbf{ABSTRACT}

Objectives. The degree and rate of photopolymerization in resin-based dental composites will significantly affect polymer network formation and resultant material properties that may determine their clinical success. This study investigates the mechanical properties, the generation of stress from polymerization, tooth cusp deflection and marginal integrity of experimental resin composites that contain different photoinitiators.

Methods. Experimental light-activated resin composites (60 vol% particulate filled in 50/50 mass% bis-GMA/TEGDMA) were formulated using a monoacylphosphine oxide (MAPO) photoinitiator and compared with a conventional camphoroquinone (CQ)-based system. Similar radiant exposure was used (18 cm\(^{-2}\)) for polymerization of each material although the curing protocol was varied (400 mW cm\(^{-2}\) for 45 s, 1500 mW cm\(^{-2}\) for 12 s and 3000 mW cm\(^{-2}\) for 6 s). Degree and rate of polymerization was calculated in real-time by near infrared spectroscopy and the generation of stress throughout polymerization measured using a cantilever beam method. Flexural strength and modulus were acquired by three-point bend tests. Standardized cavities in extract pre-molar teeth were restored with each material, the total cuspal deflection measured and post-placement marginal integrity between the tooth and restoration recorded.

Results. Generally, MAPO- exhibited a significantly higher degree of conversion (72 ± 0.8 to 82 ± 0.5%) compared with CQ-based materials (39 ± 0.7 to 65 ± 1.6%) regardless of curing protocol (p < 0.05) and MAPO-based materials exhibited less difference in conversion between the three-point bending, flexural strength and modulus tests.
curing protocols. CQ-based materials exhibited between ~85 and 95% of the maximum rate of polymerization at <15% conversion, whereas MAPO-based RBCs did not approach the maximum rate until >50% conversion. Higher irradiance polymerization had a significant deleterious effect on the mechanical properties of CQ-based materials \( (p < 0.05) \) whereas MAPO-based materials exhibited increased strength and modulus and were less affected by the curing method. Total cuspal deflection in restored extracted teeth was higher for CQ- compared with MAPO-based materials cured at the lowest irradiance curing protocol \( (12.9 \pm 4.0 \text{ and } 8.3 \pm 1.5 \mu \text{m}) \) and similar at \( 3000 \text{ mW cm}^{-1} \) for 6 s \( (10.1 \pm 3.5 \text{ and } 9.0 \pm 1.5 \mu \text{m}) \). A significant decrease in marginal integrity was observed for CQ-based RBCs cured at high irradiance for short exposure time compared with that of the MAPO-based RBC cured using a similar protocol \( (p = 0.037) \).

Significance. Polymer network formation dictates the final properties of the set composite and the use MAPO photoinitiators may provide an effective restorative material that exhibits higher curing speeds, increased degree of conversion, strength and modulus without compromise in terms of polymerization stress and marginal integrity between tooth and restoration.

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### 1. Introduction

The development of dental materials and associated technologies is often driven to satisfy the demands of the clinical practitioner to reduce chair-side operation time, rather than by sound materials science principles. One such example is the manufacture of light-curing units (LCUs) with high power outputs that are designed to significantly decrease the necessary exposure time required to effectively polymerize light-activated resin-based composite (RBC) materials.

Since the inception of visible-light cured RBCs in the 1970s [1], the power output of quartz-tungsten halogen light sources has increased from 35 to over 340 W producing LCUs that exhibit irradiance from $\sim 300$ to 3000 mW cm$^{-2}$. Although the manufacture of halogen LCUs has mostly stopped due to imminent governmental legislation banning the use of incandescent light sources, the development of light-emitting diode (LED) technology has resulted in a similar increasing trend of LCU irradiance. During the 1990s, the first LED LCU types were produced using an array of multiple diodes to deliver sufficient power since each chip only provided $\sim 0.03$–0.06 W [2,3]. Thereafter, advancements in LED technology introduced single diodes with significantly increased output power (1–15 W) and currently, LCU manufacturers build devices that contain single or multiple diodes with measured irradiances of $\sim 1500$–5000 mW cm$^{-2}$.

Photopolymerization of RBCs using extremely high irradiance is based on the premise that adequate cure can be achieved using substantially shorter exposure times (from 20 to 40 s to less than 10, but even as brief as 1 s in the case of some modern units), thereby reducing chair-side procedure time, which has been suggested to result in significant financial benefit [4]. However, for the same radiant exposure (irradiance × time), the assumption that an increase in irradiance and reciprocal decrease in cure time will lead to equivalent material properties is flawed. Material properties following photopolymerization not only rely on curing protocols, but also on intrinsic characteristics such as monomer viscosity and radical mobility and therefore, such reasoning cannot be considered as a general rule. More specifically, there exists a large body of evidence suggesting that irradiance and time independently affect the mechanical and physical properties of cured resins and RBCs [5–10]. Recent studies have also reported the significant effect of resin viscosity on polymerization kinetics of resins and RBCs cured using high irradiance [9,10]. For low viscosity (unfilled) resins containing greater than or equal to 40% diluent (TEGDMA) [9] and specific (commercial) “flowable” RBCs with low viscosity parent resin [10], “fast” high irradiance curing regimes severely limit polymer conversion. It is known that higher system mobility in less viscous media increases the probability of radical loss by bimolecular termination, and at higher irradiance that loss is greater than for similar radiant exposure achieved at lower light intensity for longer time [11]. Consequently, if “ultra-fast” (<10 s) cured composites are desirable, alternative materials chemistry should be explored that may avoid the potential for under-cured and physically inferior resin-composite restorations.

Previous work by our group has identified the potential of alternative photoinitiators, such as monoacylphosphine oxide (MAPO) that may replace camphorquinone (CQ) in contemporary RBCs [12]. MAPO is a Type I photoinitiator that does not require a co-initiator and exhibits much greater molar absorptivity and polymerization efficiency compared with CQ, which, if considered with their specific absorption range and used with a curing light that exhibits an appropriate spectral output, may allow for a reduction in curing time without significant reduction of polymer conversion at high curing light irradiance [12]. Although the degree and rate of polymer conversion determine important material properties, irradiance and exposure time are well known to independently affect polymer chain length and crosslinking, which may ultimately determine mechanical strength and stiffness and degradation of the cured RBC. Furthermore, significantly increased curing rates achieved with photoinitiators such as MAPO may decrease the ability of flow within the curing composite and increase the magnitude of stress...
resulting from polymerization, which may ultimately compromise the integrity of the tooth-restoration margin. Consequently, this work aims to determine whether the photoinitiator type and rate of polymerization affect mechanical properties, the developed stress magnitude as well as the tooth-material interface evaluated through ex vivo cuspal deflection and microleakage.

2. Experimental procedure

2.1. Materials

50/50 mass% of bisphenol-A glycidyl methacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) resins with equimolar concentrations (0.0134 mol dm$^{-3}$) of the photoinitiator, camphorquinone (CQ) and co-initiator, dimethylaminolethyl methacrylate (DAMAEMA) (0.20/0.80 mass%) or monoacylphosphine oxide (MAPO) (0.42 mass%) were mixed in a lightproof container at 60 °C for 2 h. Silanised barium silicate glass fillers (55 vol% of 1 μm and 5 vol% of 0.05 μm average diameter particles) were mixed for one minute at 2300 rpm, followed by one minute at 3500 rpm using a centrifugal mixer (Speedmixer, DAC 150, Hauschild and Co. KG, Hamm, Germany).

2.2. Curing protocol/spectral irradiance and absorption

Specimens were cured with an 11 mm diameter tip halogen Swiss Master Light (EMS, Switzerland), chosen for its broad spectrum, overlapping the absorption spectrum of both photoinitiators (albeit only partially with MAPO). Emission spectra were measured by calibrating a UV-Vis spectrometer (USB4000, Ocean Optics) using a deuterium tungsten light source (calibrated to NIST standards) with known spectral output in the UV-VIS and NIR range (Mikropack DH2000-CAL, Ocean Optics, Dunedin, USA), which allowed absolute measurements of irradiance for the light curing unit (LCU). The absorption spectra of the photoinitiators were determined in methyl methacrylate (Sigma-Aldrich, UK) using the UV-vis spectrometer coupled to a standard cuvette holder in absorbance mode. Three different curing protocols were applied to compare the applicability of exposure reciprocity law at similar radiant exposure of 18 J cm$^{-2}$: 400 mW cm$^{-2}$ for 45 s, 1500 mW cm$^{-2}$ for 12 s and 3000 mW cm$^{-2}$ for 6 s. For cuspal deflection measurements, only the extreme curing protocols were used.

2.3. Degree of conversion and rate of polymerization

Fourier Transform near infrared spectroscopy (FT-NIRS) was used to calculate polymer conversion and curing rates (Nicolet 6700, Thermo Scientific, Hemel Hemstead, UK) by monitoring the height of the peak at 6164 cm$^{-1}$, which corresponded with the vinyl $-\text{CH}_2$ absorbance [12]. Curing kinetics of the resin composites were measured for 70 s through a 12 mm $\times$ 1 mm cylindrical white Teflon mold placed on a glass slide and covered by a thin glass cover slip (n = 3).

2.4. Flexural strength properties

In order to avoid the overlapping curing regime stipulated in ISO4049: 2008 for three-point flexural strength testing, which would result in increased radiant exposure received by the irradiation overlap along 25 mm bar-shaped specimens, 12.5 mm $\times$ 1 mm $\times$ 1 mm specimens were light cured in a single-shot from a distance of 1 mm. The cured specimens were tested 24 h post-irradiation using a universal testing machine (Model 5544, Instron Ltd., High Wycombe, Bucks, England) operating at a crosshead speed of 0.75 mm/min. Each specimen was centrally loaded using a small knife-edge indenter across a 10 mm support span and the flexural strength and modulus calculated by Eqs. (1) and (2), respectively:

$$\sigma_f = \frac{3FL}{2BH^2}$$

(1)

$$E_f = \frac{FL^3}{4BH^2D}$$

(2)

where $F$ is the maximum load (N), $F_1$ is the maximum load measured at a convenient point on the straight line portion of the load-deflection trace and $D$ is the deflection of the specimen at that point (mm); $L$ is the distance, in millimeters, between the supports (10 mm); $B$ is the breadth (mm) and $H$ is the height (mm) of the specimen.

2.5. Polymerization stress

The ’Bioman’ device, designed at the University of Manchester [13], was used to evaluate the generation of stress throughout and following cure. Briefly, the apparatus consisted of a cantilever beam that embodies a 500 kg capacity load-cell and holds a steel rod (10 mm diameter, 22 mm length) perpendicular to the load-cell axis. The device was calibrated periodically using a series of calibration weights to provide a linear calibration plot of load-cell signal (mV) versus applied load (N). The resin composite specimen was introduced to the testing device on a 3 mm thick glass plate and sandwiched between this plate, via a rigid stainless steel platform (with an aperture to permit transillumination through the glass plate), and the rod, forming a 10 mm diameter by 0.8 mm thickness uncured material disk. Both the rod and glass plate surface were grit-blasted with 50 μm alumina particles to aid bonding between the rod–material–glass interfaces. Any excess material was removed and the specimen allowed to stabilize in dark conditions for 2 min at 23 °C prior to photopolymerization using the same curing protocols described in Section 2.2. Throughout polymerization, the developing stress in the constrained and shrinking specimen caused micro-displacement at the free end of the load cell, which was continually measured via the load-cell signal (N) and converted into stress (MPa) using the specimen face area. The compliance of the device remained constant throughout testing (circa 6 μm/MPa). To consider polymerization stress data that corresponded to a higher stiffness load cell and lower compliance (that might be expected in tooth cavities that have less compliance and generate more stress) a correction factor of ×4 was used [13,14].
2.6. **Cuspal deflection and microleakage**

32 maxillary premolars free from caries, hypoplastic defects or cracks were subjected to calculus deposit removal using a hand-scaler and distributed into 4 groups (n = 8); CQ-45 s@400, CQ-6s@3000, MAPO-45 s@400 and MAPO-6s@3000 mW cm⁻². The maxillary premolars were fixed into a cubic stainless steel mold and stored in 0.5% chlorine solution at 23 ± 1 °C until they were required for the extensive cavity preparation. Large standardized mesial-occlusal-distal (MOD) cavities were prepared under copious water irrigation. The width of the approximal box was two-thirds the bucco-palatal width (BPW) of the maxillary premolar, the occlusal isthmus was prepared to half the BPW and the cavity at the occlusal isthmus was standardized to a depth of 3.5 mm from the tip of the palatal cusp and 1 mm above the amelocemental junction at the cervical aspect of the approximal boxes. The cavosurface margins were all prepared at 90° and all internal line angles were rounded.

Following cavity preparation, the tooth surfaces were prepared for bonding with a three-step adhesive (All-Bond 2® Universal Adhesive System, Bisco Inc., Schaumburg, IL, USA). The MOD cavity preparation was air-dried for 30 s, prior to the application of a 32% phosphoric acid etching gel (Uni-Etch®) for 15 s without agitation before rinsing with water. Following a light drying with an air-syringe for 1 s, five consecutive coats of the primer (a mixture of All-Bond 2® Universal Dental Adhesive System Primer A (Ref B-2511, Lot 1000007217) and Primer B (Ref B-2512, Lot 1000007218)) was applied with a saturated brush tip until the surface appeared glossy. The primer mixture was lightly dried with an air-syringe for 5 s. A thin layer of bonding resin (D/E Resin, Ref B-2502A, Lot 1000007219) was applied to the primed enamel and dentin and light irradiated for 20 s with a QTH LCU (Optilux 501, Kerr Mfg. Co., Orange, CA, USA) operating in standard mode at a light intensity of 660 ± 32 mW cm⁻². Each MOD cavity was restored using an oblique incremental technique with the placement of three triangular-shaped increments (~2 mm thickness) in the mesial approximal box, three triangular-shaped increments in the distal approximal box and two occlusal increments.

A Tofflemire matrix band was shaped and placed around the maxillary teeth prior to resin composite placement and care was taken to ensure the buccal and lingual cusps of the maxillary premolar teeth were free to contact the receptors of the twin channel deflection measuring gauge (Twin Channel Analog Gauge Unit, Thomas Mercer Ltd., St. Alban’s, UK). To ensure consistency in the measuring technique, the palatal measuring gauge was placed 2.5 mm from the palatal cusp tip prior to recording the baseline cuspal deflection measurement. Following each curing protocol, deflection measurements were recorded at 180 s post-irradiation for each increment and the combined total cuspal deflection measurement (the sum of the buccal and palatal cusp deflections) was calculated for each maxillary premolar tooth.

The restored maxillary premolar teeth were polished using a slow hand-piece under water with Sof-Lex Finishing discs (3M ESPE, St. Paul, MN, USA) and 15 µm grit Composshape finishing diamond burs (Intensiv, Viganello-Lugano, Switzerland). Following polishing, the root apices of the maxillary premolar teeth were sealed with nail varnish (Rimmel 60 Seconds, London, UK) with the exception of a 1 mm band around the margins of each restoration surface. The teeth were thermocycled for 500 cycles between two water-baths maintained at 4 ± 1 °C and 65 ± 1 °C and involved submerging the teeth for 10 s in each water-bath with a 25 s transfer between water-baths. The thermocycled teeth were immediately immersed in 0.2% basic fuchsin dye for 24 h. The maxillary premolar teeth were then sectioned mid-sagittally in the mesio-distal plane using a ceramic cutting disk (Struers, Glasgow, Scotland) operating at 125 rpm under an applied load of 100 g. The sectioned teeth were examined under a stereo-microscope (Wild M3C, Heerburg, Switzerland) at 25× magnification. The extent of the cervical microleakage was recorded by assigning a score where ‘0’ was no evidence of dye penetration; a score of ‘1’ was superficial dye penetration not beyond the ADJ; a score of ‘2’ was dye penetration along the gingival floor and up to the axial wall; a score of ‘3’ was dye penetration along the axial wall and across the pulpal floor and a score of ‘4’ was dye penetration into the pulp chamber from the pulpal floor.

2.7. **Statistical analyses**

Group mean comparisons were made by two-way analysis of variance (ANOVA) for photoinitiator type and curing protocol and one-way ANOVA at a significance level of p = 0.05. Supplementary Post hoc Tukey tests were also conducted. Where necessary, a non-parametric Kruskal–Wallis test followed by pairwise group comparisons using Mann–Whitney U tests were used (p = 0.05).

3. **Results**

The absolute irradiance of the curing unit and photoinitiator molar absorptivity are presented in Fig. 1. The spectral output of the halogen lamp, designed to coincide with the absorption profile of CQ, exhibits restricted overlap with MAPO absorption. As power of the unit increases, the emission spectra widens and a greater effective irradiance with MAPO was observed.

Generally, MAPO- exhibited a higher conversion (72 ± 0.8 to 82 ± 0.5%) measured at 60 s post-irradiation compared with CQ-based materials (39 ± 0.7 to 65 ± 1.6%) regardless of curing protocol (Fig. 2; p < 0.05). The degree of conversion of MAPO-based composites cured at 3000 mW cm⁻² for 6 s was significantly greater compared with specimens cured at 400 mW cm⁻² for 45 s (p < 0.05), although conversion was less influenced by curing protocol compared with that of the CQ-based material. For CQ, the high irradiance curing regime resulted in a substantial reduction in polymer conversion compared with 1500 mW cm⁻² for 12 s and 400 mW cm⁻² for 45 s (p < 0.001).

For each curing regime, all MAPO-based resin composites exhibited a significantly higher rate of polymerization compared with CQ types (Fig. 3; p < 0.05). The maximum rate of polymerization increased and time to reach rate maxima decreased with higher irradiance regardless of the type of photoinitiator used. Fig. 4 describes the relationship of polymerization rate and degree of conversion. For CQ-based
materials, ~85–95% of the maximum rate of polymerization occurs at less than ~15% conversion, whereas MAPO-based resin composites do not approach maximum rates until greater than ~50% conversion (Fig. 4).

Fig. 5 presents the flexural strength and modulus for each material type cured using different protocols. For CQ-based composites a significant reduction in flexural strength and modulus was observed following irradiation at 3000 mW cm\(^{-1}\) for 6 s compared with both 1500 mW cm\(^{-1}\) for 12 s and 400 mW cm\(^{-1}\) for 45 s curing protocols (p < 0.05). MAPO-based materials cured at 400 mW cm\(^{-1}\) for 45 s resulted in lower strength values compared with higher irradiance protocols (p < 0.05), although flexural modulus was not affected by the curing method.

The rate of stress generation throughout cure was less for decreasing irradiance regardless of material type (Fig. 6). The magnitude of polymerization stress recorded at 60 s post-irradiation was significantly reduced for CQ-based composites cured at 3000 mW cm\(^{-1}\) for 6 s compared with both lower irradiance protocols (Table 1; p < 0.001). In contrast, MAPO-based materials exhibited higher polymerization stress at 3000 mW cm\(^{-1}\) for 6 s and 1500 mW cm\(^{-1}\) for 12 s compared with the lowest irradiance protocol (Table 1; p < 0.05). At 400 mW cm\(^{-1}\) for 45 s, the stress magnitude of MAPO- was decreased compared with CQ-based materials (p < 0.05) even though degree of conversion of the former was significantly increased (72 ± 0.8% compared with 65 ± 1.6%; Fig. 2). Further, the maximum degree of conversion achieved for CQ- (65 ± 1.6% for samples cured at 400 mW cm\(^{-1}\) for 45 s) and MAPO-based materials (82 ± 0.5% for samples cured at 3000 mW cm\(^{-1}\) for 6 s) (Fig. 2) resulted in similar polymerization stress values of 7.2 ± 0.2 and 7.0 ± 0.4 MPa, respectively (p > 0.05; Table 1).

A two-way ANOVA test of cuspal deflection revealed significant overall differences between material type and curing protocol (p < 0.05). A significant increase in total cuspal deflection was recorded for CQ-based samples at 400 mW cm\(^{-1}\) for 45 s compared with the highest irradiance protocol. The deflection measurements were significantly higher for CQ-compared with MAPO-based materials cured at the lowest irradiance curing protocol (Table 2; p < 0.05). Similar

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**Table 1** - Polymerization shrinkage stress measured following 60 s. Similar letters and numbers represent a non-significant difference in shrinkage stress in rows and columns, respectively.

<table>
<thead>
<tr>
<th>Curing protocol</th>
<th>Polymerization shrinkage stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45 s at 400 mW cm(^{-1})</td>
</tr>
<tr>
<td>CQ</td>
<td>7.2 (0.2) 1,a</td>
</tr>
<tr>
<td>MAPO</td>
<td>5.5 (0.6) 2,b</td>
</tr>
</tbody>
</table>

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**Table 2** - Total cuspal deflection of standard cavities restored with CQ- and MAPO-based resin composites. Similar letters and numbers represent a non-significant difference in shrinkage stress in rows and columns, respectively.

<table>
<thead>
<tr>
<th>Curing protocol</th>
<th>Total cuspal deflection (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45 s at 400 mW cm(^{-1})</td>
</tr>
<tr>
<td>CQ</td>
<td>12.9 (4.0) 1,a</td>
</tr>
<tr>
<td>MAPO</td>
<td>8.3 (1.5) 2,b</td>
</tr>
</tbody>
</table>
cuspal deflection measurements were recorded for both CQ- and MAPO-based composites cured at 3000 mW cm$^{-2}$ for 6 s ($p > 0.05$). Kruskal–Wallis and subsequent Mann–Whitney test revealed a significant increase in microleakage for CQ-based RBCs cured at high irradiance for short exposure time compared with that of the MAPO-based RBC cured using a similar protocol ($p = 0.037$).

4. Discussion

Although radiant exposure, that is the total energy per unit area delivered to the surface of a light curable resin (the product of irradiance and exposure time), is an important consideration, in what way the radiant exposure is acquired is probably of greater concern for final properties of the set material. For equivalent material properties, irradiance and cure time do not provide an inverse reciprocal relationship beyond a range that is dependent upon material composition. With the introduction of curing devices with ever-increasing power output there exists a real danger of placing defective resin-based materials if general dental practitioners are not adequately informed [15]. As the current results suggest, curing a conventional (CQ-based) resin composite at high irradiance for short cure times results in inferior material properties (degree of conversion, flexural strength and modulus; Figs. 2 and 5). Fig. 3 demonstrates the classic, non-steady state polymerization kinetics that is typical of highly crosslinked systems. As cure proceeds, radical mobility decreases reducing radical combination and therefore the rate of termination. The subsequent increase in radical concentration leads to an increase in the rate of polymerization (or autoacceleration). At some point during autoacceleration termination becomes diffusion controlled and instead of bimolecular termination (that is, radicals diffusing together by segmental or bulk diffusion, which is highly improbable in the highly crosslinked system being formed), radicals move by propagating through unreacted double bonds. The reaction reaches a maximum rate and begins to decrease (or autodeceleration) and occurs because high crosslinking and eventual vitrification restrict and arrest the propagation reaction limiting conversion. In the case of CQ-based RBCs cured at 3000 mW cm$^{-2}$ for 6 s, the substantially reduced conversion at similar radiant exposure ($29 \pm 0.7\%$) is a result of a decrease in polymerization growth centers at early stages of the curing reaction. At the initial stages of the reaction, higher mobility
allows for a greater probability of bi-radical termination and since radical loss is proportional to the squared concentration of radicals [11], high irradiation protocols that generate a greater number of radicals result in increased termination. Therefore, short exposure times cannot compensate for radical loss and conversion is severely limited especially in lower viscosity systems such as adhesive resins and “flowable” resin composites [10] or experimental formulations that contain bisGMA/TEGDMA ratios less than 60/40 mass% [9].

The increased rates of polymerization and degree of conversion of light-cured resins and resin composites containing MAPO photoinitiators have been reported previously [12,16–19] and are in agreement with the current findings. The molar absorptivity (Fig. 1) and quantum yield efficiency of MAPO is known to be significantly higher compared with that of CQ [20]. Further, direct photolytic cleavage of the Type I photoinitiator, MAPO provides two radicals compared with one active radical generated by CQ through indirect intermediate reaction steps of the co-initiator. MAPO-based materials exhibited less difference in degree of conversion between curing protocols compared with CQ (Fig. 2b) since the increased radical concentration was less affected by radical recombination (and increased termination rates), and an increase in the effective spectral overlap between the curing light and photoinitiator at higher power (Fig. 1).

Clearly, the significant decrease in flexural strength of CQ-based RBCs cured at 3000 mW cm⁻² for 6 s can be attributed to the significant reduction of polymer conversion for similar curing protocols (Fig. 5a). Differences in polymerization kinetics of multifunctional methacrylate resins may significantly affect polymer formation and resultant mechanical properties of the set material even though conversion is similar. The significantly decreased modulus of CQ-based materials at higher irradiance and shorter exposure times (Fig. 5b) is a result of decreased polymer crosslinking. Previous research has demonstrated that, for CQ-based resin composite materials, small differences in the degree of conversion can affect crosslink density and elastic modulus greatly [5,21]. However, similar flexural moduli of MAPO-based RBCs were observed regardless of curing protocol, which can be attributed to the nature of the photoinitiator and the effects of high cure rates on polymer formation and crosslink density.

During polymerization, shrinkage (strain) and modulus development, which are governed by conversion, contribute to the generation of stress. An increased stress development may therefore have been expected for MAPO-based materials, which exhibit significantly increased conversion, rate of polymerization and flexural modulus. However, the polymerization stress of MAPO-compared with CQ-based RBCs was either similar or reduced even at higher conversion (Fig. 6).

By plotting degree of conversion against the rate of polymerization (Fig. 4), the initial stages of vitrification can be estimated since monomer mobility is severely restricted at the point of conversion where polymerization rate begins to slow [22]. Conversion that governs shrinkage as the system vitrifies primarily contributes to stress development [23] and if greater conversion can take place prior to gelation and vitrification, polymerization stress can be reduced. Here, CQ-based materials exhibit between ~85 and 95% of the maximum rate of polymerization at less than 15% conversion, whereas MAPO-based RBCs do not approach the maximum rate until greater than 50% conversion. The conversion kinetics of each photoinitiator varies due to their differences in molar absorptivity and radical formation, which will significantly affect network formation. In the case of MAPO-based resin composites, network formation appears to delay diffusion-controlled propagation. The persistence of high system mobility until late in the reaction (illustrated by the high rate at higher DC) may explain the moderate magnitude of stress even though rate and degree of conversion is increased. In contrast, CQ-based resins exhibit gelation and vitrification at lower conversion, which has two consequences: first, it limits the final degree of conversion, and second, the majority of conversion occurs in a system with low mobility, thereby transmitting more stress. Further, the inevitable increase in exotherm and reaction temperatures associated with MAPO-based materials (and the curing unit) will allow higher reaction mobility and greater stress relief by delaying the onset of vitrification [24]. There exists a complex interaction of conversion, modulus development and stress generation. In the case of MAPO-based RBCs, the increased free volume and higher DC prior to

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**Fig. 4 – Plots of degree of conversion against rate of polymerization for (a) CQ-based, and (b) MAPO-based resin composites. Vitrification can be estimated at the point of conversion where rate begins to decelerate.**
vitrification compensates for higher modulus and final DC resulting in polymerization stress values that are at least comparable with conventional, CQ-based materials.

Similar to the in vitro stress measurements, the higher polymerization rates, conversion and modulus of MAPO compared with CQ-based RBCs were not translated as an increased cuspal deflection, which may be associated with the differences in curing characteristics identified previously. Although CQ-based RBCs exhibited relatively low conversion at high irradiance (39%), from the plot of rate vs conversion, the rate approached its maximum at early stages of the reaction providing more opportunity for stress generation and therefore increased cuspal deflection. It should be noted that any differences between in vitro stress measurements and ex vivo cuspal deflection is likely due to a difference in compliance of the test system. The extensive cavities used for the cuspal deflection measurements would provide a highly compliant system. The results and their ranking of stress and/or microleakage may significantly differ with lower compliance, for example, restoration of a deep Class I cavity. A significant increase in microleakage was observed for CQ-based RBCs cured at high irradiance for short exposure time compared with that of the MAPO-based RBC cured using a similar protocol (Fig. 7; \( p = 0.037 \)). The increased microleakage may be due
to a combination of higher cuspal deflection and therefore increased gap formation at the tooth-restoration interface and decreased polymer conversion and crosslinking of Q-based materials cured using high irradiance and short exposure time.

5. Conclusions

A reciprocal relationship between irradiance and curing time does not exist for specific compositions of light-activated dimethacrylate resin composites for any of the properties considered in this work. The use of a phosphine oxide initiator provided superior mechanical and physical properties for high irradiance curing protocols compared with materials based on camphoroquinone. Most importantly, the materials that exhibited increased degree of conversion, polymerization stress, modulus and stress magnitude did not necessarily increase cuspal deflection or have a detrimental effect on microleakage. New materials may be designed using alternative photoinitiators for ultra-fast curing that exhibit significantly improved polymer conversion and elastic modulus without significantly increasing polymerization stress, cuspal deflection, or microleakage.

REFERENCES


