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Photoinitiator type and applicability of exposure reciprocity law in filled and unfilled photoactive resins

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ABSTRACT

Objectives. To test the influence of photoinitiator type and filler particle inclusion on the validity of exposure reciprocity law.

Materials and methods. 50/50 wt% Bis-GMA/TEGDMA resins were prepared with equimolar concentrations of camphorquinone/DMAEMA (0.20/0.80 mass%) (CQ) or Lucirin-TPO (0.42 mass%), and were used either unfilled or filled to 75 mass%. Specimens were cured with a halogen Swiss Master Light (EMS, Switzerland) using four different curing protocols: 400 mW/cm^2 for 45 s as reference protocol (18 J/cm^2), 1500 mW/cm^2 for 12 s (18 J/cm^2), 3000 mW/cm^2 for 6 s (18 J/cm^2) and 3 s (9 J/cm^2). Degree of conversion (DC) was measured in real time for 70 s by FT-NIRS and temperature rise using a thermocouple. Depth of cure was determined with a penetrometer technique.

Results. With respect to DC and depth of cure, exposure reciprocity law did not hold for any tested material, except for the depth of cure of filled CQ-based materials. At similar radiant exposure, DC was significantly higher ($p < 0.05$) for all unfilled and filled TPO-based materials compared with CQ-based materials. As exposure time was reduced and irradiance increased, TPO-based materials exhibited higher DC whilst an opposite trend was observed for CQ-based materials ($p < 0.05$). For similar curing regimes, depth of cure of CQ-based materials remained significantly greater than that of TPO-based materials. Adding fillers generally reduced DC, except at higher irradiance for CQ-based materials where a positive effect was observed ($p < 0.05$).

Significance. The validity of exposure reciprocity law was dependent on several factors, among which photoinitiator type and filler content were important. Lucirin-TPO is a highly reactive and efficient photoinitiator, which may allow the potential for a reduction in curing time of TPO-based photoactive materials in thin sections.

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1. Introduction

In restorative dentistry, there exists a significant demand for reduction in curing duration to minimize chairside procedure times of multi-increment resin composite restorations. Combined with the increasing popularity and demand for photoactive resin-based restorations as a replacement for dental amalgam, major financial implications have been suggested for dentists who chose to use high power, fast curing light sources [1]. In order to achieve shorter exposure times (<10 s), whilst maintaining optimum material properties, the general trend among manufacturers has been to produce light curing units with increased irradiance. This is based on the assumption that the total energy of the irradiation, i.e. radiant exposure (J/cm^2), is the main determining factor in degree of conversion and mechanical properties of the photoactive material. As radiant exposure is the product of irradiance (I, mW/cm^2) and irradiation time (t, s), it supposed that comparable material properties result from similar radiant exposure, no matter how it is obtained (by different combinations of I and t). This is the principle known as the "exposure reciprocity law". While in certain cases this law is upheld [2–5], other studies have reported that although radiant exposure plays an important role, I and t independently influence polymer chain length, extent of crosslinking and mechanical properties, and as such, exposure reciprocity does not hold under all conditions [6–10]. A major difference among these previous citations is that some consider filled and others unfilled materials. As the experimental conditions seem critical to study exposure reciprocity law validity, it is relevant to include both classes of material in a single study, which to our knowledge has yet to be investigated.

Alternative photoinitiators have been integrated in commercially available materials in the last few years, mostly for aesthetic reasons, due to yellowing by camphorquinone/amine systems [11]. As some of these alternative photoinitiators are also interesting in terms of photopolymerization efficiency, they might also have an impact on the validity of exposure reciprocity law. Notably, Lucirin-TPO, a monoacylphosphine oxide, seems to be a promising molecule, as it presents higher molar absorptivity and curing efficiency [12,13]. However, considering the absorption characteristics of TPO and the increased scattering of light of shorter wavelength, inferior curing depth of materials that replace CQ with TPO may be a cause for concern [11]. Although recent work has highlighted the potential of TPO-based polymers to be cured in thick layers [15] and for use in dental adhesives [16], its application in filled resin composites has not been fully described. To date, the curing efficiency of TPO in filled resin-based composite has only been studied in commercial materials [11,14,17], in which TPO is not used by itself but in combination with CQ. In the latter case, lower quantum yields were measured for polymerization initiated by a mixture of TPO and CQ compared to systems in which TPO was used alone, probably due to a transfer from the more efficient photoinitiator (TPO) to the less efficient one (CQ) [18]. In addition, the exact photoinitiator concentration and ratio in commercially available composite materials is usually proprietary.

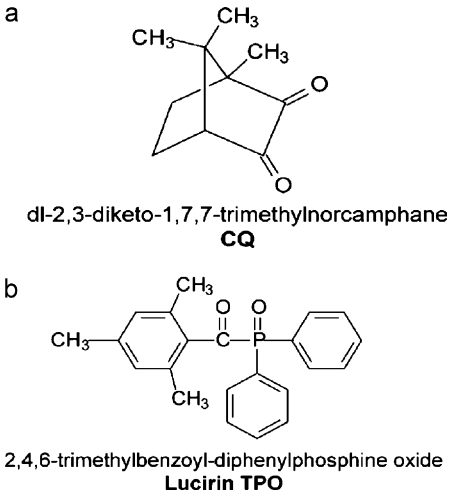

Fig. 1 – The chemical structure of the photoinitiators tested in the present study.

Consequently, the aim of this work was to investigate the impact of photoinitiator type on the polymerization efficiency in unfilled and filled experimental resins. Degree of conversion (DC) and depth of cure were measured to investigate the influence of the photoinitiator type and the presence or absence of fillers on the applicability of exposure reciprocity law.

2. Materials and methods

50/50 mass% Bis-GMA/TEGDMA resins were prepared with two different photoinitiator systems at equimolar concentration (0.0134 mol dm^{-3}): either camphorquinone (CQ), and the co-initiator, dimethylaminoethyl methacrylate (0.20/0.80 mass%) or Lucirin-TPO. The more bulky TPO structure has a molecular weight of almost twice that of CQ (348 and 166, respectively; Fig. 1) and an equimolar concentration of TPO corresponded to 0.42 mass%. The resins were tested either unfilled or filled with silanated barium glass fillers (0.7 μm) (Esschem Europe Ltd., Seaham) and fumed silica (14 nm) (Aerosil 150, Evonik Industries, Germany) to 65/10 mass%, respectively. Specimens were cured with a 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 TPO). 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 intensity of the LCU was controlled by stacking neutral density filters (Thorlabs, UK) which produced a 6-fold reduction in irradiance over the whole spectrum. 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 and another one to assess the potential of time