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Photoinitiation chemistry affects light transmission and degree of conversion of curing experimental dental resin composites

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ABSTRACT

Introduction. The effect of photoinitiator and co-initiator chemistry on the setting reaction and degree of conversion of dental resin-based composites (RBCs) has rarely been determined explicitly. This work examines the effect of type and concentration of photoinitiator and co-initiator on the rate of change of light transmission throughout polymerisation and degree of conversion of model RBC formulations.

Methods. Bisphenol-A diglycidyl ether dimethacrylate (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (6:4 molar ratio) resins filled with silanized glass filler (74 wt.%) and containing various photoinitiators (camphorquinone; CQ, 1-phenyl-1,2-propanedione; PPD, benzil; BZ), co-initiator types (*N*,*N*-dimethyl-*p*-amino benzoic acid ethyl ester; DABE, *N*,*N*-cyanoethyl methylaniline; CEMA, *N*,*N*-diethanol-*p*-toluidine; DEPT) and concentration (0.0–0.3% DABE) were polymerised using a halogen or LED light curing-unit (LCU) for 10, 20 and 40 s. The setting reaction was monitored in real-time by measuring the light transmittance through the curing specimen and bulk degree of conversion (DC) evaluated using Fourier transform infra-red spectroscopy.

Results. Specimens containing CQ and PPD cured with the halogen LCU did not have a significant *effect* on DC or changes in light transmission, although a significant increase in DC was observed for CQ compared with PPD specimens cured with the LED LCU. DABE and CEMA were more effective co-initiators than DEPT. Although DC was not limited by co-initiator concentration, the absence of a co-initiator resulted in marked differences in light transmission and decreased DC throughout 40 s irradiation with each LCU type.

Conclusions. The spectral range emitted from different types of LCU and absorption characteristics of the photoinitiator chemistry of light-activated resin-based composites play a critical role in the efficiency of polymerisation.

1. Introduction

Photopolymerisation using high-intensity visible light has been the standard setting procedure for dental resin-based composites (RBCs) for several decades. The photoinitiator chemistry of the RBC is fundamental for efficient polymerisation to achieve satisfactory mechanical and physical properties of the polymer, whereby an optimum correlation of photoinitiator absorption with the spectral emission of the dental light curing-unit will maximise the photon absorbance

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efficiency [1,2]. The majority of photoinitiator molecules formulated for dental resins consist of two-component systems: the photoinitiator which can absorb light directly and a co-initiator that does not absorb light but interacts with the activated photoinitiator to generate a reactive species (a free radical) and initiates polymerisation. Camphorquinone (CQ) is a typical visible light-activated free radical photoinitiator which exhibits an absorbance range between 400 and 500 nm (λ_{max} = 470 nm) and requires a tertiary aliphatic amine reducing agent (an electron donor), usually dimethylaminoethylmethacrylate (DMAEMA), for efficient polymerisation to occur. The type and concentration of photoinitiators and co-initiators has been extensively investigated to improve the efficacy of the setting reaction [3–6]. Exceeding a critical concentration limit of CQ, whereby unreacted molecules are not able to react with the co-initiator and return to the ground state results in yellow discolouration. This may attenuate the irradiating light and prevent formation of free radicals in deeper layers of the RBC limiting depth of cure [3,7] or result in an aesthetically undesirable restoration [4]. Consequently, "white" co-initiators, such as 2,4,6-trimethylbenzoyl-diphenylphosphine oxide (Lucerin-TPO) and 1-phenyl-1,2-propanedione (PPD) which has a maximum absorbance spectral peak in lower wavelength ranges (λ_{max} = 390 nm) have been used in combination with CQ to lessen the yellowing effect [4]. The probability of light absorption by the photoinitiator molecule is dependent upon its molar extinction coefficient (ε). Photoinitiators exhibiting higher values of ε at a specific absorption wavelength will result in an increased yield of free radicals, ultimately leading to an improved curing efficiency of the polymerisation system [8,9].

A principal disadvantage on polymerisation of RBCs remains residual shrinkage stress, which may compromise the bond between the tooth and RBC interface [10,11]. Previous studies have focussed on slowing the onset of resin gelation in an attempt to alleviate shrinkage stress by flow of the pre-gel form, whereby a decreased cure rate using an initial low light intensity followed by increased light intensity may be achieved without significantly decreasing the degree of conversion [12,13]. Additionally, differences in the intrinsic properties of monomer resin formulations have been reported to significantly reduce the rate of polymerisation [14,15]. Previous investigations have studied the effect of type and concentration of monomer and photoinitiator chemistry on the resultant shrinkage stress induced by the polymerising system [5,15].

Although polymerisation shrinkage and degree of conversion have previously been related [16–18], the associated magnitude of shrinkage stress existing at the tooth and restoration interface is a multifactorial process. Furthermore, the effect of photoinitiator and co-initiator chemistry on the polymerisation setting reaction and degree of conversion has not always been unequivocally determined. Consequently, the current investigation aims to examine the effect of type and concentration of photoinitiator and co-initiator on the rate of change of light transmission throughout polymerisation and degree of conversion of model RBC formulations.

2. Experimental procedure

2.1. *Materials*

Each experimental resin contained a mixture of bisphenol-A diglycidyl ether dimethacrylate (bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) in a molar ratio of 6:4. The photoinitiator chemistry within each resin contained either CQ, PPD or benzil (BZ) at a concentration of 0.2 wt.%. Although it was realised that the differences in molar concentration of the photoinitiators may significantly affect the concentration of free radicals, the use of standard weight percent ratios in the current study was considered reasonable since the molecular weight of the photoinitiators were similar (CQ = 166.2, PPD = 148.2, BZ = 210.2). Each resin also contained various types and concentrations of co-initiator, namely, *N*,*N*-dimethyl-*p*-amino benzoic acid ethyl ester (DABE), *N*,*N*-cyanoethyl methylaniline (CEMA) and *N*,*N*-diethanol-*p*-toluidine (DEPT) (Table 1). The initiator and co-initiators were thoroughly dissolved in the monomer resin and reinforced with silanised glass filler, added incrementally and mixed homogeneously to a 74 wt.% loading.

2.2. *Specimen preparation*

The experimental RBCs were packed into circular cavities (Ø = 4 mm) in 24 mm × 2 mm thick black Nylotron moulds. Opposing surfaces were covered with cellulose acetate strips to limit oxygen inhibition of the outer layers. Specimens from each group ($n = 3$) were irradiated for 10, 20 or 40 s using a conventional quartz–tungsten–halogen (QTH; Elipar Trilight; 3M ESPE Dental Products, St Paul, MN, USA) or first generation (19 diodes) light-emitting diode (LED; Elipar Freelight; 3M ESPE Dental Products) light curing-unit (LCU). Irradiance of the QTH and LED LCUs were 685 ± 8 and 267 ± 3 mW cm^{-2} measured at full aperture using a digital radiometer (Cure Rite; Efos Inc., Ontario, Canada). A light guide mould alignment set-up was used to allow the light guides to be positioned concentrically over each specimen thereby ensuring a nominally identical light curing procedure for all samples.

2.3. *Light transmission*

Changes in light transmission throughout polymerisation of each cylindrical specimen were recorded using an established computer-based diode technique [19,20]. An optical-electronic integrated circuit containing a photodiode and transimpedence amplifier on a single chip was utilised to determine the total irradiance transmitted through the specimens over the entire period of light activation. The incident curing light induced a current within the diode proportional to the curing-light intensity, which was interfaced with a computer and displayed at a sampling rate of 10 s^{-1}. Following analysis, each specimen was stored 'dry' in lightproof containers at 23 ± 1 °C for 48 h before evaluation of degree of conversion, in order to allow for the majority of post-irradiation or 'dark' polymerisation to take place.