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Photopolymerization of highly filled dimethacrylate-based composites using Type I or Type II photoinitiators and varying co-monomer ratios

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ABSTRACT

Objectives. The use of a Type I photoinitiator (monoacylphosphine oxide, MAPO) was described as advantageous in a model formulation, as compared to the conventional Type II photoinitiator (Camphorquinone, CQ). The aim of the present work was to study the kinetics of polymerization of various composite mixtures (20–40–60–80 mol%) of bisphenol A glycidyl dimethacrylate/triethylene glycol dimethacrylate (BisGMA/TegDMA) containing either CQ or MAPO, based on real-time measurements and on the characterization of various post-cure characteristics.

Methods. Polymerization kinetics were monitored by Fourier-transform near-infrared spectroscopy (FT-NIRS) and dielectric analysis (DEA). A range of postcure properties was also investigated.

Results. FT-NIRS and DEA proved complementary to follow the fast kinetics observed with both systems. Autodecceleration occurred after ≈1 s irradiation for MAPO-composites and ≈5–10 s for CQ-composites. Conversion decreased with increasing initial viscosity for both photoinitiating systems. However despite shorter light exposure (3 s for MAPO vs 20 s for CQ-composites), MAPO-composites yielded higher conversions for all co-monomer mixtures, except at 20 mol% BisGMA, the less viscous material. MAPO systems were associated with

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Trapped radicals
Elution

increased amounts of trapped free radicals, improved flexural strength and modulus, and reduced free monomer release for all co-monomer ratios, except at 20 mol% BisGMA.

Significance. This work confirms the major influence of the initiation system both on the conversion and network cross-linking of highly-filled composites, and further highlights the advantages of using MAPO photoinitiating systems in highly-filled dimethacrylate-based composites provided that sufficient BisGMA content (>40 mol%) and adapted light spectrum are used.

1. Introduction

The polymerization kinetics of dimethacrylate-based resins have been extensively studied, particularly in relation to their application as dental restorative materials [1,2]. For this application, there is a specific demand for fast curing, highly filled resin-based materials, which are able to withstand the mechanical demand of masticatory load and degradative effects of the aqueous and frequently acidic environment. Glass and silica particles of micron and sub-micron dimensions, surface-modified with methacryl-functional silanes have been used as reinforcing fillers within dimethacrylate resin matrices. Free radical polymerization (FRP) is commonly used in these systems, initiated by light-sensitive molecules, which in most commercially available materials is a combination of camphorquinone (CQ) and a tertiary amine (Type II system). Specific curing mechanisms have been identified, most notably an autoacceleration and autodecelaration, associated with high polymerization rates, along with diffusion controlled termination and free radical entrapment [3–6]. Such fundamental work on polymerization kinetics was carried out with spectroscopic methods, mid or near-infrared spectroscopy being the most-used, but also with calorimetric and mechanical techniques such as differential scanning calorimetry [6–8] and dynamic mechanical analysis [9]. Amongst these studies, the effects of light irradiance, resin and photoinitator chemistry have been studied.

Although previous work has provided useful information, many fundamental studies were conducted using unfilled resins, while dental restorative resin-based materials are reinforced with glass filler particulates to improve mechanical and physical material properties, typically up to 50–70 vol% (70–80 wt%) [10,11]. Few studies are available which report fundamental polymerization kinetics parameters in heavily filled resin composites. In these paste-like materials, light transport to deep layers is restricted due to, and amongst other factors, the presence of fillers and pigments, the absorption of photoinitiator molecules. Further, bulk viscosity is very high [12] and functional group conversion is lower than their resin counterparts [13].

Also, fundamental studies have focused primarily on detailing polymerization mechanisms in reactions using low light irradiance [5,14,15], (~50 mW/cm^2) in order to monitor polymerization under slower reaction rates. However, in highly filled resin composites, much higher light intensities are required to polymerize in depth [16] within acceptable curing times. Clinically relevant irradiances range from 500 to 3000 mW/cm^2, in general around 1000 mW/cm^2 used to light cure a ~2 mm thickness increment of conventional resin composite in ~20 s. Higher rates would be expected under such settings [13], affecting the polymer structure due to decreased chain length and increased amount of cross-links [17].

Furthermore, several photoinitiators (UV or visible, Type I or II) were used in the above-mentioned fundamental studies, without formal comparisons of their impact on polymerization kinetics. The Type II initiation system previously mentioned (CQ) absorbs in the visible range (400–500 nm; λ_{max} = 470 nm), while Type I molecules such as acylphosphine oxides absorb in the UV–vis region (λ_{max} ~380 nm) with a much higher absorption efficiency and radical yield [18,19]. Most interestingly for dental materials, their use in model dental resin-based composites led to shorter curing times (3–10 s [20], compared to 20 s with CQ). Several studies by our group focused on a model composite to compare the use of either a Type I (phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide, MAPO) or a Type II (CQ) photoinitiating system [13,21–23]. The Type I-based composite presented faster kinetics under short irradiation times (1–3 s) and improved functional group conversion, reduced monomer elution and improved mechanical properties.

However the effect of such a potentially useful photoinitiation system within resins of varying viscosity is unknown. Further, determining the influence of kinetics on the formation of a cross-linked polymer network is also important to determine the effect of network structure on resulting mechanical properties.

Consequently, the aim here was to study the kinetics of polymerization of a series of BisGMA/TegDMA formulations, using either MAPO or CQ-based resins filled to 75 wt%. The study of polymerization kinetics will be the first objective of the present work and achieved by use of complementary methods adapted to appropriately follow fast polymerizations, i.e. near-IR spectrometry and dielectric analysis (DEA). These methods will be discussed with regard to their suitability to follow ultra-fast polymerizations. The second objective will be to further characterize the resulting polymer network of the cured materials by measuring elastic modulus and flexural strength by three-point bending, free monomer elution by reverse phase high pressure liquid chromatography (HPLC) and trapped free radicals by electron paramagnetic resonance (EPR).