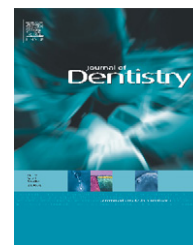


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## Onium salt improves the polymerization kinetics in an experimental dental adhesive resin

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### ABSTRACT

The aim of this study was to evaluate the influence of an onium salt in the polymerization kinetics of a dental adhesive model resin. A monomer mixture, based on Bis-GMA, TEGDMA and HEMA, was used as a model dental adhesive resin, which was polymerized using camphorquinone (CQ) as a photo-initiator in addition to either binary or ternary photo-initiator systems. The binary systems were formulated with different concentrations of diphenyliodonium hexafluorophosphate or ethyl 4-dimethylaminobenzoate in relation to the monomer and 1 mol% of CQ. The ternary system was a blend of 1 mol% of CQ, 2 mol% of ethyl 4-dimethylamino benzoate and 0.25, 0.5, 1, 2 or 4 mol% of onium salt. Real time Fourier Transform infrared spectroscopy was used to investigate the polymerization reaction over the photo-activation time. When CQ was used as photo-initiator, a slow polymerization reaction was observed and a lower monomer conversion. The addition of a second component (onium salt or amine) increases the polymerization rate and conversion independent on the co-initiator concentration. Ternary photo-initiator system showed an improvement on the polymerization rate of the dental adhesive model resin leading to high conversion in short photo-activation time. Also, a mechanism for initiating polymerization using an amine or onium salt as a co-initiator component is proposed.

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## 1. Introduction

Diaryliodonium salts, with a complex metal halide as a weakly nucleophilic counterion, are efficient photo-initiators for cationically mediated polymerization. The very low bond energy of the C–I bond (between 26 and 27 kcal/mol) allows, when light irradiated, the decomposition of the excited iodonium to an aryl iodo radical-cation, a reactive aryl radical and an anion.<sup>1</sup> Most of these photo-initiators are active when irradiated in a light range below 300 nm, therefore, UV light sources are used. Although this activation strategy is

satisfactory in some applications, such as paints and coatings, the use of UV light is not recommended in the biological field. However, it is possible that using dyes that absorb in the visible light region as sensitizers, would allow a reaction with the onium salts, promoting decomposition.<sup>2</sup> In this way, it is possible that onium salts can also act in the radical polymerization of methacrylates.<sup>3</sup> Several kinds of visible light sensitizer dyes have been investigated, such as safranine,<sup>4</sup> acridine derivatives<sup>3</sup> and acetophenone dyes.<sup>2</sup>

In the development of dental adhesives, there are three important reasons to use an onium salt: water-solubility, due

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its ionic character that can promote the polymerization of hydrophilic monomers in dental adhesives when phase-separation occurs<sup>5</sup>; compatibility with epoxy-based resin composites<sup>6</sup>; the significant increase on the polymerization rate<sup>4</sup> which is very important in systems that need a fast cure.

It is hypothesized that camphorquinone, a dye widely used as a photo-initiator for radical polymerization in dental materials, can act as a photo-sensitizer to diphenyliodonium hexafluorophosphate, which does not absorb light in the visible region, improving the reactivity of the photo-initiator system.

The aim of this study is to evaluate the influence of an onium salt on the polymerization kinetics of an experimental dental adhesive model resin. Real time infrared spectroscopy was performed and the effect of the onium salt and tertiary amine concentration was investigated.

## 2. Method and material

### 2.1. Reagents

Bisphenol A glycidyl dimethacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA), 2-hydroxyethyl methacrylate (HEMA) and camphorquinone (CQ) were supplied by Esstech Inc. (Essington, PA, USA) and used without further purification. Ethyl 4-dimethylaminobenzoate (EDAB) and diphenyliodonium hexafluorophosphate (DPIHFP) were purchased from Aldrich Chemical Co (Milwaukee, WI, USA) and used without further processing. To perform the monomer photo-activation, a halogen light-activation unit (XL 3000, 3 M ESPE, St. Paul, MN, USA) was used and the irradiation value ( $700 \text{ mW/cm}^2$ ) was confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA).

### 2.2. Formulations

A model dental adhesive resin was formulated through intensive mixing of 50 wt.% bis-GMA, 25 wt.% TEGDMA and 25 wt.% HEMA. CQ was added at 1 mol% for all groups, according to the monomer moles. Four initiator systems were investigated at various levels: 1 mol% of CQ; 1 mol% of CQ and DPIHFP (0.25, 0.5, 1, 2 and 4 mol%); 1 mol% of CQ and EDAB (0.25, 0.5, 1, 2 and 4 mol%); 1 mol% CQ + 2 mol% EDAB and DPIHFP at different molar concentrations. No radical scavenger was added to avoid interference on the polymerization kinetics.

### 2.3. Kinetics of polymerization by RT-FTIR spectroscopy

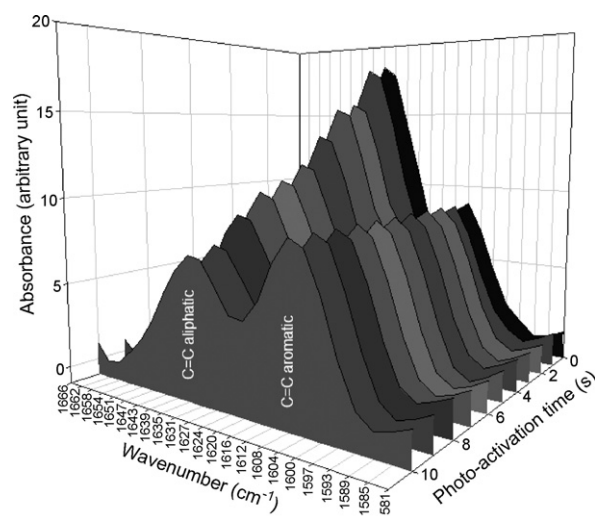
The degree of conversion from the experimental materials was evaluated using real time Fourier Transform infrared spectroscopy with a Shimadzu Prestige21 spectrometer, equipped with an attenuated total reflectance device. The reflectance device was composed of a horizontal ZnSe crystal, with a  $45^\circ$  mirror angle (PIKE Technologies, Madison, WI, USA). A support was coupled to the spectrometer, fixing the light curing unit in place and standardizing the distance between the fiber tip and the sample at 5 mm. The IRSolution software (SHIMADZU, Columbia, MD, USA) was used in the monitoring scan mode, using the Happ-Genzel apodization, at a range of

1750 and  $1550 \text{ cm}^{-1}$ , resolution of  $8 \text{ cm}^{-1}$  and mirror speed of  $2.8 \text{ mm/s}$ . With this setup, one scan every 1 s during photo-activation was acquired. Analysis was performed at a controlled room temperature of  $23^\circ\text{C}$  ( $\pm 2^\circ\text{C}$ ) and 60% ( $\pm 5\%$ ) relative humidity. The sample ( $3 \mu\text{L}$ ) was directly dispensed on the ZnSe crystal and photo-activation was performed for 60 s. The degree of conversion was calculated as described in a previous study,<sup>7</sup> considering the intensity of carbon-carbon double bond stretching vibrations (peak height) at  $1635 \text{ cm}^{-1}$  and using the symmetric ring stretching at  $1610 \text{ cm}^{-1}$  from the polymerized and non-polymerized samples as an internal standard. Data were plotted and curve fitting performed by Hill three parameter non-linear regression. Using these data, the polymerization rate ( $R_p$  ( $\text{s}^{-1}$ )) was calculated as the degree of conversion at time  $t$  subtracted of degree of conversion at time  $t - 1$ . The coefficient of determination was greater than 0.98 for all curves.

## 3. Results

In Fig. 1, typical RT-FTIR spectra in the region of  $1550\text{--}1750 \text{ cm}^{-1}$  of a photo-initiated polymerization shows the disappearance of the aliphatic carbon-carbon double bond at  $1650 \text{ cm}^{-1}$  as a function of the photo-activation time. The influence of different initiator systems on the kinetics of the photo-polymerization is presented in Fig. 2. The effect of a co-initiator dramatically reduced the photo-activation time required to reach a higher conversion when compared with the system without a co-initiator (1 mol% of CQ). Fig. 3 shows the polymerization rate profiles from the dental adhesive model resin with different co-initiator systems. When only 1 mol% of CQ was used, the maximum rate of polymerization ( $R_p^{\text{max}}$  ( $\text{s}^{-1}$ )) values were very low (in fact, undetectable), however, for the ternary photo-initiator system, the  $R_p^{\text{max}}$  was 66% higher than the CQ-EDAB system.

When amine was used as a co-initiator, the  $R_p^{\text{max}}$  values were 1.33, 1.74, 1.57 and 1.65% per second for 0.25, 0.5, 1 and



**Fig. 1** – RT-FTIR spectra in the region ( $1550\text{--}1750 \text{ cm}^{-1}$ ) for a photo-polymerization reaction as function of the photo-activation time.

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