Photoinitiator Effect in Degradation Studies of Model Dentin Adhesives

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Statement of Purpose:
The breakdown of the bond between the tooth and composite has been linked to the failure of our current adhesives to consistently seal and adhere to the dentin [1]. Results from both in vitro and in vivo studies indicate that adhesive failure allows bacterial enzymes, oral fluids, and even bacteria to infiltrate the spaces between the tooth and composite [2]. The penetration of these agents into the spaces between the tooth and composite undermines the restoration and leads to recurrent caries, hypersensitivity, and pulpal inflammation [3]. Thus the adhesive/dentin bond can be regarded as the first defense against substances that may penetrate and ultimately undermine the composite restoration in vivo. The long-term success of clinical composite restorations depends in part upon complete and appropriate polymerization. Efficient photoinitiators have been regarded as a basic requirement for complete polymerization, especially for deep cavities [4,5]. However, the conventional photoinitiator systems used in the dentin adhesive, such as those containing camphorquinone (CQ) combined with a co-initiator aromatic amine (EDMAB or DHEPT), tend to be relatively hydrophobic. The objective of this work was to combine hydrophobic/hydrophilic initiators in the adhesive resin cured under wet bonding conditions to provide greater stability during biodegradation.

Methods:
The model resin consisted of hydroxyethylmethacrylate (HEMA, Acros Organics, NJ, USA) and 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]-propane (BisGMA, Polysciences Inc., Washington, PA, USA) at mass ratios of HEMA/BisGMA 45/55. Distilled water at concentrations of 8 and 12wt% was selectively added into these neat resins. The following photoinitiators (all from Aldrich, Milwaukee, WI, USA) were selectively used in the study: camphorquinone (CQ) as a hydrophobic photosensitizer, 3-(3,4-dimethyl-9-oxo-9H-thioxanthen-2-yloxy)-2-hydroxypropyl] trimethyl ammonium chloride (QTX) as a hydrophilic photosensitizer, ethyl-4-(dimethylamino)benzoate (EDMAB) as a hydrophobic co-initiator, 2-(dimethylamino) ethyl methacrylate (DMAEMA) as a hydrophilic co-initiator, and diphenyliodonium hexafluorophosphate (DPIHP) as the iodonium salt (hydrophilic). After a three day pre-wash, adhesive discs were incubated with/without porcine liver esterase (PLE) in phosphate buffer (PB, pH 7.4) at 37°C. Supernatants were collected daily and analyzed for MAA and HEMA by HPLC.

Results:
The hydrophobic photoinitiators, CQ and EDMAB, have lower solubility in water than the more hydrophilic photoinitiators such as QTX, DMAEMA and DPIHP. Solubilities of CQ and EDMAB are greatest in the relatively hydrophobic HEMA/BisGMA mixtures, as expected, while the solubilities of DMAEMA and DPIHP are relatively unaffected by a change in hydrophobicity. On exposure to PLE, the net cumulative MAA release for adhesive formulated with the more hydrophilic initiators and polymerized in water was significantly decreased ($p < 0.05$) relative to the control specimens containing hydrophobic initiators (Fig 1).

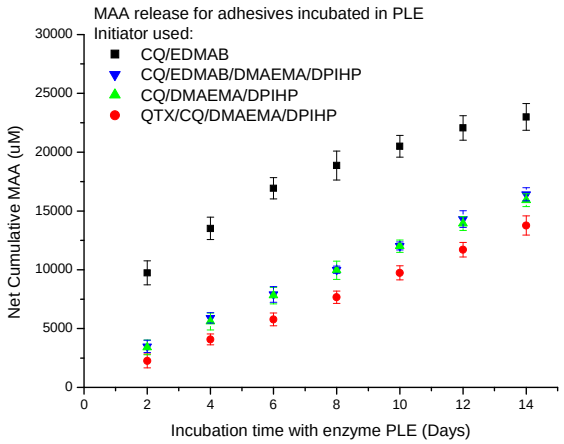

Figure 1. The cumulative release of MAA from model adhesive simulating wet bonding in the presence of PLE.

Conclusions:
For model adhesive resins photopolymerized in the presence of water, the inclusion of hydrophilic photoinitiators show greater resistance to esterase degradation without sacrificing polymerization conversion. The addition of a hydrophilic component to photoinitiator systems may reduce the detrimental effects of micro-level phase separation on the performance of these adhesives by promoting polymerization of both hydrophilic and hydrophobic domains. Designing initiator systems to perform in this heterogeneous wet environment of the oral cavity may improve the long-term performance of dentin adhesives.

References:
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