Hydrophilic-rich Phase Mimic in Dental Adhesive: Polymerization- and Solvent-Induced Phase Separation

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Statement of Purpose: Under *in vivo* conditions, the hydrophobic and hydrophilic composition of dentin adhesives can lead to phase separation which compromises the integrity of the adhesive/dentin bond.[1] The separated phases can be broadly categorized into hydrophobic-rich resin and hydrophilic-rich aqueous phases. If the hydrophilic-rich phase that arises due to phase separation fails to undergo substantial polymerization, the functional groups in the system become trapped as residual monomers and unreacted pendant radicals. [2,3] These unreacted monomers will be leached and such leaching has been associated with cytotoxicity. The objective of this study was to determine the photo-polymerization kinetics of model hydrophilic-rich phases of dental adhesive as a function of water content. In situ monitoring of the polymerization kinetics of model hydrophilic-rich phase was completed for the first time. We hypothesize that the minimum rate of polymerization will occur at a critical concentration of water.

Methods: Adhesive formulations containing bisphenol-A diglycidyl ether dimethacrylate (bisGMA, Polysciences, Warrington, PA), 2-hydroxyethyl methacrylate (HEMA, Acros Organics, NJ) were photo-polymerized in the presence of water (D_2O). Model hydrophilic-rich phase mimics were made from HEMA/BisGMA neat resins containing 95 and 99 wt% HEMA, respectively. The formulations are shown in a ternary phase diagram[4] (Fig.1). Degree of conversion and polymerization kinetics were determined by a Perkin-Elmer Spectrum 400 Fourier transform infrared spectrophotometer (FTIR) with a Time-resolved spectrum collector (PerkinElmer™ Spectrum TimeBase). Viscosity was measured at various shear rates using a Brookfield DV-II+Pro viscometer in a cone/plate setup. Modulated Temperature DSC (MTDSC) was carried out using TA instruments model DSC Q200.

Results: All of the samples exhibited two-stage polymerization behavior which has not been reported previously for dental resin formulations. Minimum secondary rate maxima were observed for water content of 10-30%wt. Viscosity decreased with increased water content. Differential scanning calorimetry (DSC) showed two glass transition temperatures for the hydrophilic-rich phase of dental adhesive. The DSC results indicate that the heterogeneity within the final polymer structure decreased with increased water content. The results suggest a reaction mechanism involving both polymerization-induced phase separation (PIPs) and solvent-induced phase separation (SIPs) for the model hydrophilic-rich phase of dental resin.

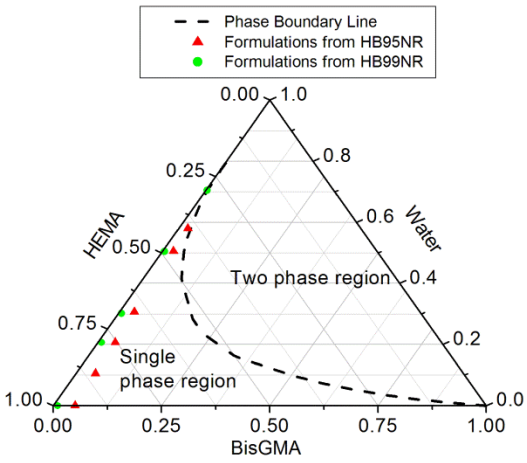

Figure 1. Ternary phase diagram for water, BisGMA and HEMA. The dashed line exhibits the phase boundary line. The filled triangles and circles represent formulations made from neat resins- HB95NR and HB99NR respectively.

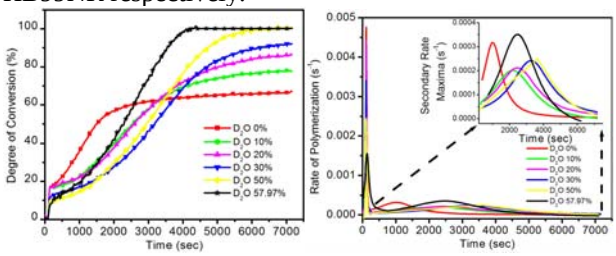

Figure 2: Degree of conversion (left) and rate of polymerization (right) of formulations made from neat resin containing 95wt% HEMA for varying D2O content.

Conclusions: Although all model hydrophilic-rich phase exhibit substantial degree of conversion in presence of sufficient photo-initiator, the resultant polymer will be loosely cross-linked due to the limited amount of the critical dimethacrylate, BisGMA. This will allow oral fluid to enter into the dentin/adhesive interface facilitating hydrolytic and enzymatic degradation of the dental polymer. [4]

References:

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Acknowledgement: Supported by grant R01DE143923 (PS) and R01DE022054 (PS, JSL), from the NIDCR/NIH, Bethesda, MD 20892.