Photo-polymerization Kinetics of Hydrophilic-rich Phase Mimic in Dentin Adhesive

Q. Ye[1], F. Abedin[1], P. Spencer[1,2], R. Parthasarathy[1], A. Misra[1,3], J. S. Laurence[1,4]
[1]University of Kansas Bioengineering Research Center, [2]University of Kansas, Department of Mechanical Engineering
[3]University of Kansas, Department of Civil Engineering, , [4]University of Kansas, Department of Pharmaceutical Chemistry

Statement of Purpose: The breakdown of the tooth/composite bond has been linked to the failure of current adhesives to provide a durable seal at the interface with dentin. Water is a major interfering factor when bonding adhesives and/or composite to the tooth. Previous studies have revealed sensitivity issues of current dentin adhesives to over-wet conditions. Phase separation in the presence of excess moisture limits infiltration of the cross-linkable dimethacrylate monomers and hydrophobic photo-initiators into demineralized dentin matrix [1]. We have recently determined the near-equilibrium partition of hydrophobic/hydrophilic components – monomers and initiators of dentin adhesive when exposed to wet environments simulating the oral cavity [2,3]. Present investigation involves polymerization kinetics study of hydrophilic-rich phase mimic at miscibility limit with water. The objective of this work was to further investigate the polymerization behavior of the hydrophilic-rich phase in adhesive that undergo phase separation under wet, oral conditions.

Methods: Experimental adhesives 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 close to the miscibility limit. Model hydrophilic-rich phase mimics investigated here were made from HEMA/BisGMA neat resins containing 95, 99, 99.5 and 100 wt% HEMA, respectively. These samples (HB95PB, HB99PB, HB99.5PB and HB100PB) contained maximum single-phase water content (e.g., at the phase boundary) were formulated with either standard photoinitiator concentration or reduced photoinitiator concentration. 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.

Results: The viscosity and polymerization kinetics of hydrophilic-rich phase were significantly different from those of hydrophobic-rich phase (Fig. 1). Hydrophobic-rich phase undergoes autoacceleration immediately following exposure to visible light, but the hydrophilic-rich phase exhibits delayed post-polymerization at much later stage. Model hydrophilic-rich phases with reduced photo-initiator content (Fig. 2) exhibit limited polymerization, whereas with sufficient photo-initiator content they show substantial polymerization, which is important to limit monomer leaching.

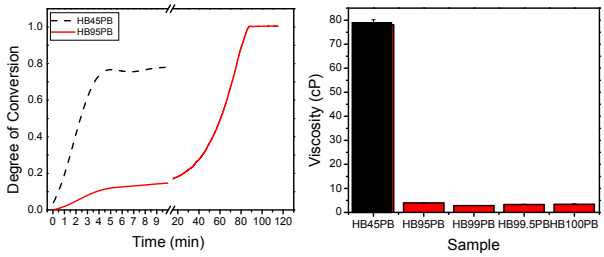

Figure 1. Viscosity and polymerization kinetics of hydrophobic & hydrophilic-rich phases.

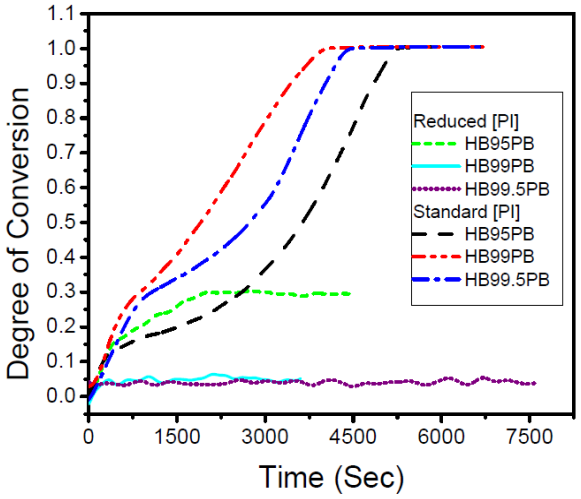

Figure 2. Polymerization kinetics study with standard vs. reduced photo-initiator concentration

Conclusions: On interaction with the water from demineralized dentin, the components of the adhesive phase separate due to their different viscosity and miscibility. The hydrophilic-rich phases at miscibility limit are able to undergo substantial polymerization given sufficient photo-initiator. In order to ensure significant polymerization of the hydrophilic-rich phase under clinical condition, it is important to optimize photo-initiator in the current dentin adhesive to include hydrophilic photo-initiator components [4].

References:

1. Spencer P, Wang Y. J Biomed Mater Res 2002, 62:447
2. Ye Q et al. J Dent Res 2011, 90(12):1434-1438
3. Ye Q et al. J Biomed Mater Res Part B 2012, 100B:1086-1092
4. Ye Q et al. Dent Mater 2009, 25:452-458

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