

Correlation between Photo-Polymerization behavior and Microstructure of Heterogeneous Model Dentin Adhesive

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Statement of Purpose: Under *in vivo* conditions, there is little control over the amount of water left on the tooth during dentin bonding [1]. As a result, it is possible to leave the dentin surface so wet that the adhesive actually undergoes physical separation into hydrophobic and hydrophilic-rich phases [2]. Because water is ubiquitous in the mouths of healthy patients, it is important to understand the role of adhesive phase separation on the structure/property relationships of these materials. The purpose of this investigation was to determine the correlation between polymerization characteristics, thermal/mechanical properties and phase-contrast features of model nanophase-separated dentin adhesive.

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 0, 5, 10, and 16 wt% was selectively added into these neat resins. The photoinitiators camphorquinone (CQ), ethyl-4-(dimethylamino) benzoate (EDMAB) were obtained from Aldrich (Milwaukee, WI, USA). The model adhesives were light-cured for 20s using a dental curing light (Spectrum® 800) operated at 550 mW/cm². The photo-polymerization of the model adhesives during irradiation was monitored *in situ* using a Perkin-Elmer Spectrum One Fourier transform infrared spectrophotometer (FTIR) with a resolution of 4 cm⁻¹ in the ATR sampling mode. A novel time-based spectrum collector (PerkinElmer™ Spectrum TimeBase) was used to offer continuous and automatic collection of IR spectra during adhesive polymerization. The degree of conversion (DC) was calculated based on the time-dependent decrease in the absorption intensity band ratios before and after light curing. Polymer structure was revealed by thermal behavior in the glass transition temperature (T_g) region; these measurements were obtained by modulated DSC (Q100, TA Instruments). The phase contrast images were obtained using a Nanoscope IIIa scanning probe microscope (Digital Instruments, Santa Barbara, CA) operated in tapping mode according to the techniques published previously [3]. The modulus of elasticity of polymerized beam specimens (1x1x11 mm) was determined by 4-point bend tester (Deben 2KN, UK).

Results:

There was little difference in the degree of conversion (DC) of model dentin adhesives cured in the presence of water concentrations ranging from 0-16 wt%, but there were substantial differences in the polymerization kinetics, glass transition temperature, phase structure and mechanical properties. Bimodal polymerization rates were easily found in the more dilute resin system due to a

delayed onset of diffusion limitation and autoacceleration as shown in Fig. 1. DC values at rate shoulder and maxima are around 10% and 30%, respectively, regardless of the water concentration. Two glass transition temperatures are noted, one associated with the loosely crosslinked and the other with the densely crosslinked region; the difference between these two temperatures corresponded with the heterogeneity of the adhesive. The maximum polymerization rate decreased with the increased water concentration and corresponded with the second glass transition temperature showing the overall crosslink density of model adhesives and their elastic modulus values. Phase contrast became evident with the increase of water concentration in the initial adhesive formulation.

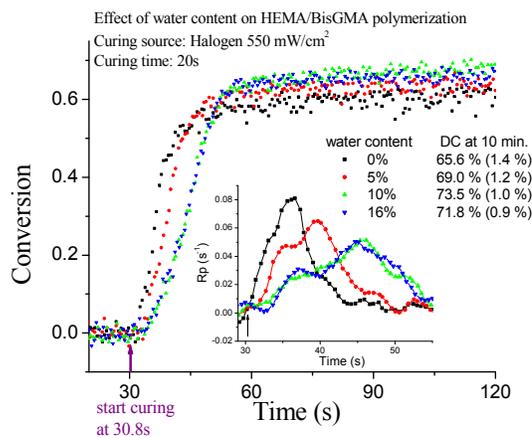


Figure 1. Photopolymerization kinetics of model dentin adhesive cured in the presence of water.

Conclusions:

The bimodal polymerization rate, double T_g, and the nano-heterogeneous structure of photo-polymerized dentin adhesive were correlated. The water in the adhesive formulation influenced the polymerization kinetics, lowered the second glass transition temperature suggesting reduced crosslink density and elastic modulus of cured copolymer network. Water within the oral environment could have a similar detrimental effect and thus, the structural integrity of these materials would be impacted adversely.

References:

1. Kugel G, et al., JADA 2000, 131, 20s.
2. Spencer P, Wang Y. J. Biomed. Mater. Res. 2002, 62, 447.
3. Ye Q, et al, J. Appl. Polym. Sci. 2007, 106, 3843.

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