

Effect of water on photopolymerization and properties of dentin adhesives with branched methacrylate

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Statement of Purpose: Photopolymerizable methacrylate polymers are used as dentin adhesives; these materials serve to bond a composite resin to the tooth structure. Photopolymerizable biomaterials such as methacrylates are especially advantageous as dentin adhesives due to flexibility in material design and ease of handling. However, since (meth)acrylate-based polymer networks have numerous ester groups that are subject to chemical and enzymatic hydrolysis in the biological environment of the wet oral cavity. These hydrolytic reactions may lead to premature degradation of the adhesive and ultimately the composite restoration. The overall objective of this work is to develop new methacrylate-based dentin adhesives that show improved durability in the moist environment of the mouth while retaining the desirable handling characteristics, mechanical properties, adhesive penetration, esthetic character and low toxicity of the methacrylates. The threefold purpose of this investigation was: to prepare a new dentin adhesive containing a multifunctional methacrylate-based monomer with a branched side chain; to characterize the structure/property relationships, and to evaluate the water-compatibility and esterase-resistance of this new adhesive.

Methods: The new monomer, trimethylolpropane mono allyl ether dimethacrylate (TMPEDMA), was synthesized by the reaction of trimethylolpropane mono allyl ether and methacryloyl chloride. The synthesized TMPEDMA was identified by ¹H-NMR and ¹³C-NMR spectroscopies. The new experimental adhesives, TMPEDMA/HEMA/BisGMA= 25/45/30 w/w ratio were formulated with H₂O (wt%) at: 0, 8 and 16% water (A0T, A8T, A16T, respectively). The control adhesives consisted of HEMA and BisGMA with a mass ratio of 45/55 and were formulated with water (0, 8 and 16 wt% A00, A08 and A16, respectively). Camphoroquinone (CQ) and 2-(dimethylamino)ethyl methacrylate, and diphenyliodonium hexafluorophosphate were used as the photoinitiator system.

Degree of conversion (DC), tensile and thermal properties, and adhesive penetration were determined. 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 for 8 days. Supernatants were collected daily and analyzed for MAA and HEMA by HPLC.

Results: DC (Fig 1), mechanical and thermal properties and adhesive penetration were comparable for the control and experimental adhesives. The levels of analytes HEMA in PB or MAA in PLE were increased in A08 and A16 as compared to A00, which suggests that there could be a greater loss of material in HEMA/bisGMA adhesives that experience phase separation under wet bonding conditions. On exposure to PLE, the net cumulative

MAA release for adhesive discs formulated with the new monomer and polymerized in water was significantly decreased ($p < 0.05$) relative to the control specimens containing only HEMA and BisGMA (Fig 2).

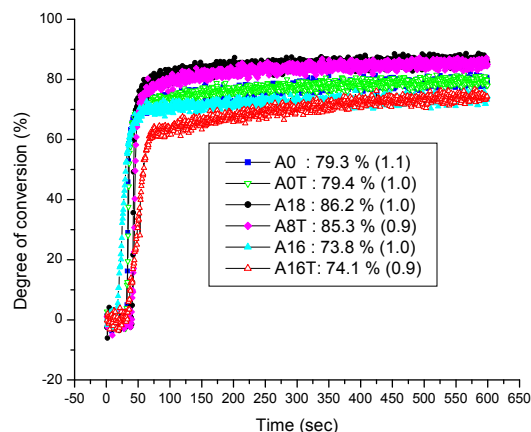


Fig. 1. Degree of initial double bond conversion of adhesives as a function of time from 0 to 600 sec. All samples were cured with 550 mW/cm² for 20 s at 25 °C.

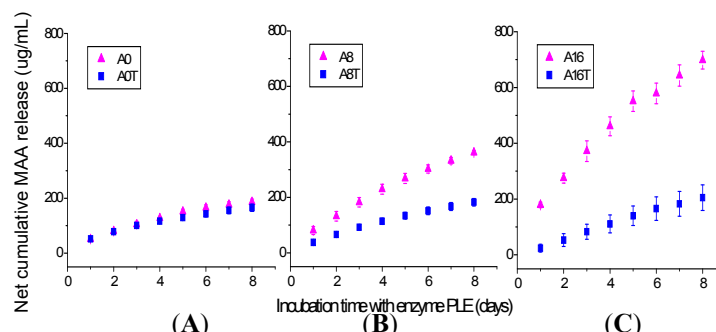


Figure 2. Net cumulative MAA release from control and experimental adhesives [A0 vs. A0T (A); A8 vs. A8T (B); A16 vs. A16T (C)] Using ANOVA together with Tukey's test at $\alpha=0.05$ the results show statistically significantly less MAA release with experimental adhesive formulated in water.

Conclusions: When polymerized in the presence of water, dentin adhesives that include a new monomer with branched linkage show greater resistance to esterase degradation without sacrificing DC, adhesive penetration or mechanical properties. These results suggest better esterase resistance of the adhesive formulated with the new monomer and prepared under wet conditions that simulate the oral environment.

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