**Preparation and properties of novel methacrylate-based dentin adhesives with esterase resistance**

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**Introduction:** The widespread use of dental restorative composites has been stimulated by the public's concern about mercury release from dental amalgam and the need for improved aesthetic dental restorations[1]. However, the failure rate for large to moderate posterior composite restorations can be 2-3 times that of high copper amalgam[2]. The premature failure of the composite restorations can be traced to a breakdown of the bond at the tooth surface/composite interface[2]. One of the reasons connected with the breakdown of the bond at the interface is degradation of dental resins in human saliva, leading to a decrease in mechanical strength and surface hardness[3]. Yourtee *et al.* have demonstrated that dimethacylate containing aromatic functional groups or branched methacrylate linkages show greater degradation resistance[4]. The aim of this study was to synthesize and characterize a new dimethacrylate monomer with a branched side chain for use as a comonomer in dentin adhesives, and to evaluate the properties of adhesives.

**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 (Figure 1) was identified by FTIR, $^{1}$H-NMR and $^{13}$C-NMR spectroscopies. HEMA/BisGMA=45/55 (A00) and HEMA/BisGMA /TMPEDMA=45/30/25 (A25T) w/w ratio were formulated. Camphoroquinone (CQ) and 2-(dimethylamino)ethyl methacrylate were used as the photoinitiator system. The degree of conversion (DC) of the adhesives was determined using FTIR/ATR with curing times of 20 sec. Each adhesive was polymerized with visible light at 550 mW/cm$^2$ and test specimens exposed to a 3-day pre-wash with 1 mL phosphate buffer (PB) for biodegradation. Following the pre-wash, adhesive discs were incubated with/without porcine liver esterase (PLE, EC 3.1.1.1, 30 U/mL) at 37$^{o}$C. Supernatants were collected daily and analyzed for methacrylic acid (MAA) and 2-hydroxyethyl methacrylate (HEMA) by HPLC with UV-detection at 208 nm up to 8 days. Mechanical tests for properties were performed using a Debon four-point bending tester. Thermal tests were carried out to determine the glass transition temperature (Tg) using a TA Instruments Modulated DSC Q100.

**Results/Discussion:** Spectral data of TMPEDMA are as follows: $^{1}$H-NMR ($CDCl_3$): δ6.0 and 5.0 ppm ($C\underline{H}_2$=C($CH_3$)COO-), 5.7-5.8 ($CH_2$=C$\underline{H}$-$CH_2$O-), 5.1-5.2 ($C\underline{H}_2$=CH-$CH_2$O-), 4.1 (-$CH_2$=C($CH_3$)COO$C\underline{H}_2$-), 3.9 ($CH_2$=CH-$C\underline{H}_2$O-), 3.3 ($CH_2$=CH-$CH_2OC\underline{H}_2$-), 1.9 (-$CH_2$=C($C\underline{H}_3$)COO-), 1.4-1.5 ($CH_3C\underline{H}_2$C-), 0.8-0.9 ($C\underline{H}_3CH_2$C-); FTIR (neat): 1718.5 cm$^{-1}$ (C=O, stretching of methacrylate), 1637.9 cm$^{-1}$ (C=C, stretching), 1158.4 cm$^{-1}$ (C-O, stretching). At curing times of 20 s, the degree of conversion (DC) was nearly identical for A00 (79.3%) and A25T (79.4%). The modulus of elasticity and Tg were 1.65 GPa and 118$^{o}$C for A00 and 2.0 GPa and 130 $^{o}$C for A25T, respectively. The higher mechanical and thermal properties of the model adhesive, A25T, may be due to increased crosslink density promoted by the multifunctionality of new monomer. Both adhesives released significantly higher levels of MAA on day-1 compared to other days. The net cumulative release of MAA in the presence of enzyme was similar for both adhesives prior to the 4$^{th}$ day. After that time, A25T showed decreased degradation in the enzyme-rich environment. These findings suggest improved esterase resistance in the new formulation as compared to the control.

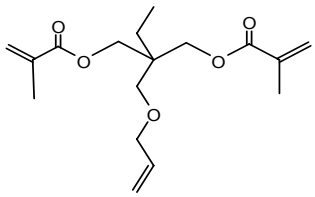

Figure 1. TMPEDMA

**Conclusions:** When model adhesive, HEMA/BisGMA was partially replaced by the new comonomer, the degree of conversion remained high (>75%), and the modulus of elasticity and glass transition temperature were improved as compared to the control. The incubations of adhesives with PLE showed that after the fourth day, A25T showed decreased degradation in the enzyme which may be due to the steric hindrance of branched alkyl side chain and/or increased crosslink density of a new monomer against enzymatic hydrolysis. Supported NIH/NIDCR R01 DE14392.

**References:**

1. Peutzfeldt A. Eur J Oral Sci 1997;105:97-116.
2. Collins C.J. J Dent 1998; 26:311-317.
3. Larsen IB. J Dent Res 1991; 99:254-261.
4. Yourtee D.M. J Biomed Mater Res 2001; 57:522-531.