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Synthesis and evaluation of novel siloxane-methacrylate monomers used as dentin adhesives

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ABSTRACT

Objectives. The objectives of this study were to synthesize two new siloxane-methacrylate (SM) monomers for application in dentin adhesives and to investigate the influence of different functionality of the siloxane-containing monomers on the adhesive photopolymerization, water sorption, and mechanical properties.

Methods. Two siloxane-methacrylate monomers (SM1 and SM2) with four and eight methacrylate groups were synthesized. Dentin adhesives containing BisGMA, HEMA and the siloxane-methacrylate monomers were photo-polymerized. The experimental adhesives were compared with the control adhesive (HEMA/BisGMA, 45/55, w/w) and characterized with regard to degree of conversion (DC), water miscibility of the liquid resin, water sorption and dynamic mechanical analysis (DMA).

Results. The experimental adhesives exhibited improved water miscibility as compared to the control. When cured in the presence of 12 wt% water to simulate the wet environment of the mouth, the SM-containing adhesives showed DC comparable to the control. The experimental adhesives showed higher rubbery modulus than the control under dry conditions. Under wet conditions, the mechanical properties of the formulations containing SM monomer with increased functionality were comparable with the control, even with more water sorption.

Significance. The concentration and functionality of the newly synthesized siloxane-methacrylate monomers affected the water miscibility, water sorption and mechanical properties of the adhesives. The experimental adhesives show improved water compatibility compared with the control. The mechanical properties were enhanced with an increase of the functionality of the siloxane-containing monomers. The results provide critical structure/property relationships and important information for future development of durable, versatile siloxane-containing dentin adhesives.

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1. Introduction

During the last 20 years, the primary motivation for changing the resin chemistry of restorative composites was to reduce the polymerization shrinkage [1]. The polymerization shrinkage occurs during the curing of the composite in the tooth cavity and may lead to the formation of marginal gaps. The silorane-based composite, introduced by 3M in 2007, exhibits the lowest polymerization shrinkage (1.4 vol%) of the current composite restorative materials [1,2].

The hybrid monomer systems introduced by 3M contain both siloxane and oxirane structural units. The main benefits of these resins are the very low polymerization shrinkage, the good biocompatibility, the very low water solubility of the monomers, and low water sorption of the formed polymer networks [3–6]. This siloxane-based composite does not, however, exhibit the lowest polymerization stress [1,2]. Other limitations, including increased exothermic effect (twice as high as dimethacrylate-based composites with similar filler load), the delay in establishing mechanical properties comparable to dimethacrylates, and the lower refractive index, have inhibited broad market acceptance of the silorane-based composite [1,7,8]. The lower bond strength of the silorane composite with commercial dentin adhesives [9] has raised concerns about the compatibility of these materials.

Siloxane-containing materials have been widely used as biomaterials in medical and pharmaceutical applications, due to their biocompatibility and low toxicity [10–13]. For example, polysiloxane has a high refractive index and can be used as the accommodating intraocular lens by the polymerization of siloxane-methacrylate monomers [14]. Siloxane-containing cross-linking agents are often used in drug delivery systems [15]. Moreover, in the presence of siloxane groups, the stability of restorative materials can be improved [16]. In this context, if siloxane groups could be incorporated into the dentin adhesive, it is expected that the durability of the dentin adhesives and compatibility with the silorane composite would be improved. However, polymers with siloxane groups are usually soft, and their mechanical strength may be low because of the flexibility of the siloxane groups [17–19]. Therefore, modification of siloxane with methacrylate to take advantage of both the stability of siloxane groups and good mechanical properties of methacrylates could be a solution.

The twofold objectives of this work were: (1) to synthesize and characterize two new siloxane-methacrylate monomers with four and eight methacrylate groups and (2) to investigate the influence of chemical structure of siloxane-containing monomers used in dentin adhesives on the following properties: degree of conversion, water miscibility, water sorption and dynamic mechanical properties. To our knowledge, this investigation marks the first study of siloxane-methacrylate monomers used in dentin adhesives. The results provide critical structure/property relationships for siloxane-methacrylate monomers and important information for future development of durable, versatile siloxane-containing dentin adhesives.

2. Materials and methods

2.1. Materials

2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (BisGMA, Polysciences, Warrington, PA) and 2-hydroxyethylmethacrylate (HEMA, Acros Organics, NJ) were used as received without further purification, as monomers in dentin adhesives. Two siloxane methacrylate monomers (SM1 and SM2) were synthesized in our lab. The control adhesive resin consisted of HEMA and BisGMA with a mass ratio of 45/55. This control was used to compare with the experimental adhesive resins with HEMA/BisGMA/SM = 45/55 – x/x (w/w) ratio. The control and experimental adhesives were also formulated with 12 wt% water to simulate bonding in the mouth. The concentration of water was based on the total final weight of the adhesive resin. Camphorquinone (CQ, 0.5 wt%), ethyl-4-(dimethylamino)benzoate (EDMAB, 0.5 wt%) and diphenyliodonium hexafluorophosphate (DPIHP, 1.0 wt%) were obtained from Aldrich (Milwaukee, WI, USA) and used as a three-component-photoinitiator system without further purification. 2,4,6,8-Tetramethyl-2,4,6,8-tetrakis(propyl glycidyl ether)cyclotetrasiloxane (TPGTS), glycerol dimethacrylate (GDMA, assay 85%, mixture of isomers), ethyl acetate, boron trifluoride diethyl etherate ($\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$), anhydrous magnesium sulfate (MgSO_4), and all other chemicals were purchased from Sigma–Aldrich at reagent grade and used without further purification.

2.2. Synthesis of siloxane-methacrylate (SM) monomers

2,4,6,8-Tetramethyl-2,4,6,8-tetrakis(propyl glycidyl ether)cyclotetrasiloxane (TPGTS, 10 g, 0.0143 mol), 2-hydroxyethylmethacrylate (HEMA, 10 g, 0.076 mol) or glycerol dimethacrylate (GDMA, mixture of isomers, 13.75 g, 0.06 mol) and ethyl acetate (EA, 100 mL) were mixed together. Boron trifluoride diethyl etherate (0.2 mL) was added into this solution. The reaction was allowed to continue at room temperature for about 12 h, and it was monitored by thin layer chromatography (mobile phase: dichloromethane/hexane, 50/50, wt%). The product-containing solution was washed with distilled water and dried over anhydrous MgSO_4 . The solvent was removed with a rotary evaporator at 35–40 °C. The process for the synthesis of the two siloxane methacrylate monomers (SM1 and SM2) is shown in Scheme 1. The yields of SM1 and SM2, which were colorless and viscous, were 92.4% and 95.0%, respectively. The structure of the synthesized compounds (SM1, SM2) was confirmed using FTIR (Spectrum 400, Perkin-Elmer, Waltham, MA), ^1H NMR and ^{13}C NMR (FT-400 MHz Bruker Spectrometer, DMSO as solvent) spectroscopies.

2.3. Preparation of adhesive formulations

The preparation of the control adhesive formulations has been reported [20,21]. As shown in Table 1, the control adhesive formulation (C0) consisted of HEMA and BisGMA with a mass ratio of 45/55 [21–23] which is similar to widely used commercial dentin adhesives. In the experimental adhesive

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