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Synthesis of none Bisphenol A structure dimethacrylate monomer and characterization for dental composite applications

*Xiaoxu Liang, Fang Liu, Jingwei He**

College of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China

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ABSTRACT

Objective. In this study, new dimethacrylate monomer SiMA without Bisphenol A (BPA) structure was synthesized and used as base resin of dental composite materials with the aim of reducing human exposure to BPA derivatives.

Methods. SiMA was synthesized through ring-opening addition reaction between 1,3-bis[2(3,4-epoxycyclohex-1-yl)ethyl]tetra-methyldisiloxane and methacrylic acid, and its structure was confirmed by FT-IR and ^{1}H NMR spectra. SiMA was mixed with TEGDMA (50/50, wt/wt) and photoinitiation system (0.7 wt% of CQ and 0.7 wt% of DMAEMA) to form resin system. Experimental composite EC was then prepared by SiMA based resin loading with $BaAlSiO_2$ microfillers (72 wt%). Double bond conversion (DC) was determined by FT-IR analysis. Volume shrinkage (VS) was measured through variation of density before and after irradiation. Water sorption (WS) and solubility (SL) were obtained until the mass variation of polymer in distilled water kept stable. Flexural strength (FS) and modulus (FM) of the polymer were measured using a three-point bending set up. Extract of composite was used to evaluate its cytotoxic effect on humane dental pulp cells, and relative growth rate (RGR) was obtained by CCK-8 assay. Bis-GMA/TEGDMA (50/50, wt/wt) resin system and universal dental restorative materials 3 M ESPE Filtek^{TM} Z250 were used as references for neat resin system and composite material, respectively.

Results. FT-IR and ^{1}H NMR spectra showed that structure of SiMA was the same as designed. For the neat resin systems: DC of SiMA based resin was higher than that of Bis-GMA based resin ($p < 0.05$); SiMA based resin had lower VS than Bis-GMA based resin; WS of SiMA based resin was lower than that of Bis-GMA based resin ($p < 0.05$), while SL of SiMA based resin was nearly the same as that of Bis-GMA based resin ($p > 0.05$); FS and FM of SiMA based resin were lower than those of Bis-GMA based resin ($p < 0.05$). For the composite materials: DC of EC was higher than that of Z250 ($p < 0.05$); EC and Z250 had same VS; WS of EC was lower than that of Z250 ($p < 0.05$), and SL of EC was higher than that of Z250 ($p < 0.05$); FS and FM of EC were lower than those of Z250 ($p < 0.05$); RGRs of EC were lower than those of Z250 after the cells were incubated with relative extract for 24 h and 48 h ($p < 0.05$), while after being incubated for 72 h, RGR of EC and Z250 had no obvious difference ($p > 0.05$).

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* *Corresponding author.*
E-mail address: msjwhe@scut.edu.cn (J. He).

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Significance. SiMA had potential to replace Bis-GMA as base resin of dental composite materials. However, formulation of SiMA based resin and composite should be optimized in terms of mechanical strength to satisfy the requirements of resin based dental materials for clinical application.

1. Introduction

As a great revolution, resin-based dental composites were first introduced to dentistry more than 50 years ago. After more than 50 years' revolution, resin-based composites have been used for a variety of applications in dentistry, such as restorative materials, cavity liners, pit and fissure sealants, crowns, orthodontic devices, endodontic sealers, and so on [1].

Resin composites usually consists of dimethacrylate based resin matrix, photoinitiator system, and coupling agent treated inorganic fillers. Though resin composites have advantages like excellent esthetic quality and relatively easy handling [2], there are still many properties need to be improved including their polymerization shrinkage, water solubility, and relative lower mechanical properties [3–8]. Moreover, dental materials that contain Bisphenol A (BPA) derivatives, such as 2,2-bis[4-(2′-hydroxy-3′-methacryloyloxy-propoxy)phenyl]propane (Bis-GMA), 2,2-di(4-methacryloxyphenyl)propane (Bis-DMA), and ethoxylated bisphenol-A-dimethacrylate (Bis-EMA), have become a problem need to be worried, because BPA has been detected to be released out of these materials [9–13]. BPA has already been reported as one of many endocrine disrupting compounds [14], and to be responsible for male reproductive abnormalities [15,16], spermatogenesis impairment [17,18], and some other diseases [19]. Therefore, in order to minimize human exposure to BPA in dental materials as a health precaution, using monomers without BPA structure is still an effective way.

In this research, a new dimethacrylate monomer SiMA without BPA structure was synthesized and used as base resin of dental composite material. Properties of neat resin system and composites with SiMA were all investigated. Bis-GMA/triethylene glycol dimethacrylate (TEGDMA) (50/50, wt/wt) resin system was used as control for neat resin, commercial dental restorative materials 3 M ESPE Filtek^{TM} Z250 was used as control for composite materials. The hypothesis is that the properties of SiMA containing material like double bond conversion, polymerization shrinkage, mechanical property, water sorption and solubility could be comparable to these properties of Bis-GMA containing material.

2. Materials and methods

2.1. Materials

1,3-Bis[2(3,4-epoxycyclohex-1-yl)ethyl]tetramethyldisiloxane (Siepoxy) was purchased from Fluorochem Ltd., UK. Bis-GMA, TEGDMA, 2-(N,N-dimethylamino) ethyl-methacrylate (DMAEMA) and methacryloxypropyltrimethoxysilane (MPS) were purchased from Aldrich Chemical Co., USA. Methacrylic acid was purchased from Guangzhou Chemical Reagent Co. Ltd., China. N,N-Dimethylbenzylamine was purchased from Shanghai No. 3 Chemical Reagent Co. Ltd., China. Anhydrous magnesium sulfate were purchased from Shanghai No. 1 Chemical Reagent Co. Ltd., China. Sodium hydroxide, dichloromethane and hydroquinone were obtained from Tianjin Chemical Reagent Co. Ltd., China. Hydrochloric acid was obtained from Guangzhou Donghong Chemical Co. Ltd., China. Camphoroquinone (CQ) was obtained from Alfa Aesar Co., USA. 3 M ESPE Filtek^{TM} Z250 was obtained from 3 M Co., USA. $BaAlSiO_2$ microfillers (average particle diameter 0.4 μm, SP345) were obtained from Specialty Glass Inc., USA.

2.2. Synthesis of dimethacrylate monomer SiMA

A mixture of Siepoxy (25.00 g, 6.5×10^{-2} mol), methacrylic acid (11.62 g, 13.5×10^{-2} mol), N,N-dimethylbenzylamine (0.366 g, 2.71×10^{-3} mol), and hydroquinone (0.183 g, 1.67×10^{-3} mol) were stirred at 90 °C for 7 h. Dichloromethane (150 mL) was then added to the reaction mixture. The resulting solution was washed successively with 0.5 mol/L aqueous HCl solution to remove N,N-dimethylbenzylamine, and 1.5 mol/L aqueous NaOH solution to remove excess methacrylic acid and hydroquinone. The organic layer was then dried overnight with anhydrous magnesium sulfate. After removing the drying agent by filtration, the dichloromethane was removed by distillation under vacuum and SiMA was obtained as light brown viscous liquid (24.05 g, 75%). Fourier Transform Infrared (FT-IR) spectrum (Vector33 Model FT-IR instrument, Bruker Co., Germany) and ^1H NMR spectrum (Avance AV 400 MHz instrument, Bruker Co., Switzerland) were taken to confirm the structure of SiMA. The results of spectroscopic studied for SiMA are as follows: IR (neat): ν (cm^{-1}) 3447, 2922, 2856, 1718, 1637, 1577, 1253, 1063, 843, 796. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.13, 5.59, 4.82–4.92, 3.80–3.90, 3.65, 1.28–1.97, 0.51–0.55, 0.62.

2.3. Silanization of $BaAlSiO_2$ microfillers

The surface of the $BaAlSiO_2$ microfillers was treated with MPS using the method reported previously [20,21]. The fillers 20 g, MPS 0.62 g, cyclohexane 200 mL and *n*-propylamine 0.13 g were stirred at 30 °C for 30 min, then kept at 60 °C for another 30 min. The mixture was placed in a rotary evaporator at 60 °C for removing the solvent and volatile by-products. The powder was then heated at 95 ± 5 °C for 1 h in a rotary evaporator and finally was dried at 80 °C in a vacuum oven for 20 h.