DENTAL MATERIALS 31 (2015) 575–582

Available online at www.sciencedirect.com

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journal homepage: www.intl.elsevierhealth.com/journals/dema

Preparation of antibacterial and radio-opaque dental resin with new polymerizable quaternary ammonium monomer

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ARTICLE INFO

Article history:
Received 24 August 2014
Received in revised form
3 December 2014
Accepted 10 February 2015

Keywords:
Dental resin
Synthesis
Antibacterial activity
Radio-opacity
Double bond conversion
Mechanical property
Polymerization shrinkage

ABSTRACT

Objective. A new polymerizable quaternary ammonium monomer (IPhene) with iodine anion was synthesized and incorporated into Bis-GMA/TEGDMA (50/50, wt/wt) to prepare antibacterial and radio-opaque dental resin.

Methods. IPhene was synthesized through a 2-steps reaction route, and its structure was confirmed by FT-IR and ^{1}H-NMR spectra. IPhene was incorporated into Bis-GMA/TEGDMA (50/50, wt/wt) with a series of mass fraction (from 10 wt.% to 40 wt.%). Degree of monomer conversion (DC) was determined by FT-IR analysis. Polymerization shrinkage was determined according to the variation of density before and after polymerization. The flexural strength, modulus of elasticity, and fracture energy were measured using a three-point bending set up. Radiograph was taken to evaluate the radio-opacity of the polymer. A single-species biofilm model with *Streptococcus mutans* (*S. mutans*) as the tests organism was used to evaluate the antibacterial activity of the polymer. Bis-GMA/TEGDMA resin system without IPhene was used as a control group.

Results. FT-IR and ^{1}H-NMR spectra of IPhene revealed that IPhene was the same as the designed structure. ANOVA analysis showed that when mass fraction of IPhene was more than 10 wt.%, the obtained resin formulation had lower DC, polymerization shrinkage, FS, and FM than control resin ($p < 0.05$). Polymers with 20 wt.% and 30 wt.% IPhene had higher fracture energies than control polymer ($p < 0.05$). IPhene containing samples had higher radio-opacity than control group ($p < 0.05$), and radio-opacity of IPhene containing sample increased with the increasing of IPhene mass fraction ($p < 0.05$). Only polymers with 30 wt.% and 40 wt.% of IPhene showed antibacterial activity ($p < 0.05$).

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http://dx.doi.org/10.1016/j.dental.2015.02.007

Significance. IPhene could endow dental resin with both antibacterial and radio-opaque activity when IPhene reached 30 wt.% or more. Though sample with 30 wt.% of IPhene had lower FS and FM than control group, its lower volumetric shrinkage, higher fracture energy, higher radio-opacity, and antibacterial activity still made it having potential to be used in dentistry.

1. Introduction

Dental composites, which consist of resin matrix and inorganic filler, are popular restorative materials because of their natural tooth color and direct-filling capabilities [1]. Dental composites have been reported to be used in more than 95% of all anterior tooth direct restorations and in about 50% of all posterior tooth direct restorations [2]. However, dental composite restorative materials have been reported to accumulate more bacteria or plaque than other restorative materials in vitro [3–6] or in vivo [7,8] because of their lack of antibacterial activity, and bacteria or plaque accumulation adjacent to the restoration margins may lead to secondary caries in vivo and shorten the life of composite restoration.

Quaternary ammonium compounds, which are active against a broad spectrum of micro-organisms such as Gram-positive and Gram-negative bacteria, fungi, and certain types of viruses [9], are well known antibacterial agents and have already been used in fields like water treatment, medicine, food applications, and textile products [9–11]. Quaternary ammonium compounds with polymerizable groups can immobilize the antibacterial quaternary ammonium group into the polymer backbone and give long-term antibacterial activity to the polymer [12]. In dentistry, Imazato firstly applied a polymerizable quaternary ammonium named methacryloyloxydodecyl-pridinium bromide (MDPB) as an antibacterial agent to prepare long-term antibacterial dental restorative materials [13–16].

Besides the antibacterial activity, quaternary ammonium compounds with iodine anion (I^-) also have radio-opacity [17], which is an important property for dental materials, because of the high electronic density of iodine [18,19]. Though radio-opacity of dental materials can be implemented by adding radio-opaque inorganic fillers, there still exist some dental materials like E-glass fiber reinforced composites and flowable resin composites that have insufficient radio-opacity [20]. Therefore, radio-opaque dental resin can be used to solve this problem.

In our previous study, a polymerizable quaternary ammonium named 2-dimethyl-2-dodecyl-1-methacryloxyethyl ammonium iodine (DDMAI) was synthesized and used to prepare antibacterial and radio-opaque dental resin system [17]. Unfortunately, DDMAI had miscible problem with hydrophobic methacrylate monomer tri-ethyleneglycol dimethacrylate (TEGDMA), and only 5 wt.% of DDMAI could be added into 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)-phenyl]propane (Bis-GMA)/TEGDMA resin system. Thus, the antibacterial activity and radio-opacity of DDAMI containing polymer were not obvious.

In this work, a new polymerizable quaternary ammonium monomer (IPhene) with iodine anion was synthesized and incorporated into Bis-GMA/TEGDMA dental resin with different mass ratio. The hypotheses are (I): IPhene could be mixed well with Bis-GMA/TEGDMA at high mass ratio; (II): IPhene could endow Bis-GMA/TEGDMA with both antibacterial and radio-opaque activity. Double bond conversion, polymerization shrinkage, flexural strength and modulus, antibacterial activity, radio-opacity of IPhene containing resin formulations were investigated and compared with resin formulation without IPhene.

2. Materials and methods

2.1. Materials

N-methyl diethanol amine (MDEA), 1-iodododecane, dibutyltin dilaurate (DBTDL), TEGDMA, camphoroquinone (CQ), N,N′-dimethylaminoethylmethacrylate (DMAEMA), and 3-isopropenyl-α,α-dimethylbenzyl isocyanate (IDI) were purchased from Sigma–Aldrich Co. (St Luois, MO, USA). Bis-GMA was applied from Esstech Inc. (Essington, PA, USA). All of the compounds were used without further purification.

2.2. Methods

2.2.1. Synthesis of polymerizable quaternary ammonium monomer (IPhene)

As shown in Fig. 1, IPhene was synthesized through a 2-steps route. FT-IR (Spectrum One, Perkin-Elmer, Waltham, MA, USA) and ^{1}H-NMR (AV 400 MHz, Bruker Co., Germany) spectra of intermediate products and IPhene were obtained to confirm their structures. The FT-IR spectra were recorded with 32 scans at a resolution of 4 cm^{-1}. The chemical shifts of ^{1}H-NMR spectra were reported in ppm on δ scale with tetramethylsilane as the internal reference and $CDCl_3$ as the solvent.

2.2.1.1. Synthesis of intermediate product N,N-bis(2-hydroxyethyl)-N-methyldodecyl ammonium iodide (HQAI-12). A mixture of MDEA (0.05 mol), 1-iodododecane (0.051 mol), and 30 mL acetone were stirred at reflux. After 24 h reaction, the acetone was removed by distillation under vacuum. The obtained raw product was washed with ethyl ether and filtered for several times. Then the white intermediate product HQAI-12 was dried under vacuum at 35 °C for 48 h. The results of spectroscopic studies for HQAI-12 are as follows: IR (neat): ν (cm^{-1}) 3294, 2956, 2927, 2855, 1381, 1090, 720. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 4.22, 4.09, 3.77–3.89, 3.57–3.62, 3.38, 1.80, 1.31–1.42, 0.94–0.95.