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Physical and chemical properties of model composites containing quaternary ammonium methacrylates

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ABSTRACT

Objective. Investigate physical and chemical properties of model composites formulated with quaternary ammonium salt monomers (QAS) at different concentrations and alkyl chains lengths

Methods. QAS with 12 dimethylaminododecyl methacrylate (DMADDM) and 16 dimethylaminohexadecyl methacrylate (DMAHDM) chains lengths were synthesized and incorporated at 5 and 10% in model composites, resulting in four groups: G12.5 (DMADDM 5%), G12.10 (DMADDM 10%), G16.5 (DMAHDM 5%), G16.10 (DMAHDM 10%). One group was used as control group (CG 0%). Degree of conversion (DC); water sorption (WS) and solubility (SL); hygroscopic expansion (HE); degradation temperature (DT); glass transition temperature (T_g) and polymerization shrinkage (PS) were determined. Knoop hardness (KNH), flexural strength (FS) and elastic modulus (EM) were measured before and after storage Data were submitted to ANOVA and Tukey's test ($p \leq 0.05$).

Results. DC ranged between 76.1 (G12.10) and 70.7 (G16.5) %; CG had the lowest WS, SL and HE. There was no statistical difference for PS and FS. KHN values ranged between 30.2 (GC) and 25 (G16.10) and after storage the performance was depended on QAS concentration and chain length. For EM, CG had the highest values before and after storage and no difference was observed in the QAS groups before storage. After storage, the results were dependent on QAS concentration (3.5-4.3 GPa).

Significance. In general, the addition of QAS increased composite's degradation compared with the CG. In the tested QAS, the addition of DMADDM at 5% concentration resulted in a less degradable material.

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1. Introduction

Due to their versatility, composites are widely used in Dentistry for direct restoration [1,2]. Although mechanical properties have been significantly improved in the last decades [1], restorative composites still present a series of shortcomings. Basically, these materials tend to accumulate more plaque than other restoratives materials due to the degradation process of the organic content and in the interface with reinforcing fillers [3]. Therefore, control of bacterial growth could be a strategy to increase their clinical lifetime [4]. Several compounds have been added to composites resin with this aim [5–8] but, in general, these combinations are not copolymerized with the resin matrix and over time could weaken the polymer matrix [9].

The use of polymerizable quaternary ammonium salts monomers (QAS) could be an interesting approach to improve materials' ability to control bacterial growth. QAS do not lose its antibacterial properties over time because it might be copolymerized with the monomers commonly used in the formulation of commercially available materials [9]. The antibacterial activity is provided by contact and would cause bacteriolysis by binding the cell membrane, resulting in cytoplasmic leakage [10,11]. Previous studies have shown excellent antibacterial properties of this antibacterial monomers [11–18], even after 6 months of storage [19]. Regarding to cytotoxicity, previous studies reported that quaternary ammonium monomers were similar to a commercially available adhesive system [20] and less toxic than BIS-GMA [13,16].

Alkyl chain length is one factor that influences the QAS antibacterial ability. In previous studies [12–14,17,18] an increase in antibacterial efficiency was observed by increasing chain length from 3 to 16, but it decreased when reached 18. Among QAS, previous studies have demonstrated elevated bactericidal efficiency of methacrylates compounds DMADDM (dimethylaminododecyl methacrylate) and DMAHDM (dimethylaminohexadecyl methacrylate) [13,14,17] with alkyl chain length of 12 and 16 respectively. Besides the chains lengths, by increasing QAS concentration the antibacterial ability of composites is elevated [12,14,15].

Until now, experimental studies have focused on the antibacterial properties of DMADDM and DMAHDM [14,16,17] and it is necessary to determine if the addition of these monomers would influence composite's overall physical and chemical properties. It was previously reported that QAS might possess hydrophilic characteristics [21], which can increase degradation. Despite scarce, there are studies available on mechanical properties [17,18], but other compounds were added to act in synergism with the QAS, thus, making it impossible to determine the real influence of DMADDM and DMAHDM on these properties.

Due to the lack of data, the aim of this study was to determine the influence of the addition of antibacterial monomer QAS (DMADDM or DMAHDM) on the physical and chemical properties of model composites at different concentrations. It was determined specifically (1) degree of conversion; (2) sorption and solubility; (3) hygroscopic expansion; (4) polymerization shrinkage; (5) thermal properties (6) Knoop hardness before and after storage in ethanol; (7) flexural properties before and after storage in water. The research hypothesis was that the addition of QAS in model composites, regardless of concentration, does not influence the variables tested.

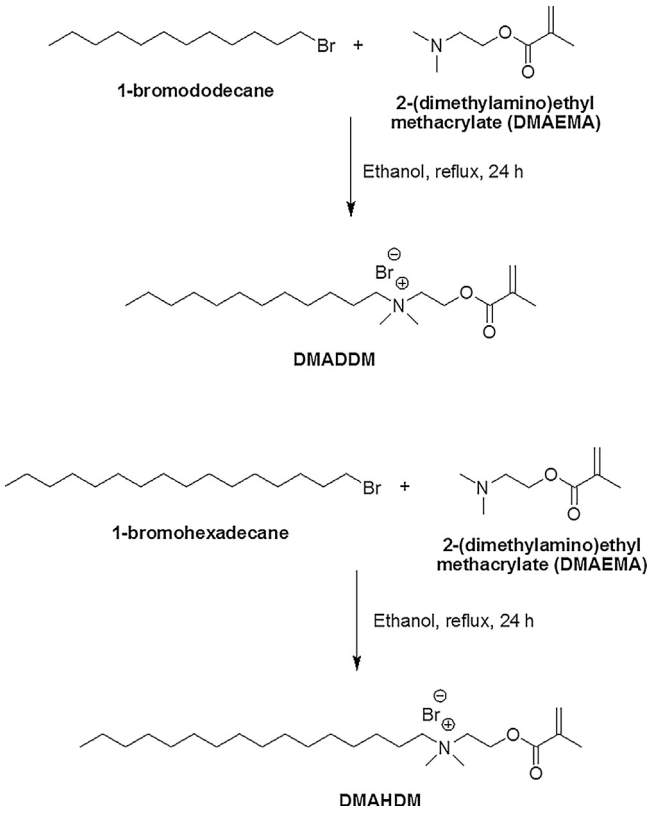

Fig. 1 – Synthesis of antimicrobial monomers DMADDM and DMAHDM.

2. Materials and methods

2.1. Synthesis of antimicrobial monomers

The antimicrobial monomers were synthesized using the Menschutkin reaction, as previously reported [14]. In this addition reaction, a tertiary amine and an organo-halide were added, in equal amounts (60 mmol), into a round bottom flask coupled to a condenser with 20 mL of ethanol and were refluxed for 24 h. After that, the solvent was evaporated to dryness (rotary evaporator) to afford the pure monomer, which did not require any purification. For each monomer, a different organo-halide was used (Fig. 1), and the tertiary amine was always 2-(dimethylamino)ethyl methacrylate (DMAEMA).

To characterize the reaction products, Nuclear Magnetic Resonance (NMR) Spectroscopy and High-Resolution Mass Spectrometry (HRMS) were used. ^{1}H and ^{13}C NMR spectra were recorded on an Avance 200 MHz spectrometer (Bruker, Billerica, MA, USA), using $CDCl_3$ as the solvent. Standard Bruker software was used throughout and chemical shifts were given in ppm (δ scale) and coupling constants (J) were given in hertz (Hz). High-resolution mass spectra were obtained on a Bruker microTOF II mass spectrometer using ESI.

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