Research Paper

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Effect of Inorganic Content on Thermal Stability and Antimicrobial Properties of Inorganic-Organic Hybrid Dimethacrylate Resins

Chemistry

KEYWORDS : inorganic-organic hybrid resins, thermal stability, antimicrobial properties, sol-gel, 3-trimethoxysilyl propyl methacrylate

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ABSTRACT

Novel inorganic-organic hybrid resins synthesized through sol-gel seek great attention due to versatility of its applications in various fields. In this work, novel inorganic-organic hybrid resins containing of alkoxides of calcium, magnesium and zinc with polymerizabledimethacrylate groups was synthesized using 3-trimethoxysilyl propyl methacrylate as the precursor. The objective of the present study was to investigate the effect of inorganic content on thermal stability and antimicrobial properties of the novel inorganic-organic hybrid resins.

Introduction

Inorganic-organic hybrid resins have wide range of applications in the field of microelectronics, wear-resistant coating, micro-optics, electro-optics, encapsulations, satellite devices, photonics, as matrices for dental composites and biomedical applications due to their good physico-mechanical properties, biocompatibility, heat dissipation, low thermal expansion and light weight [1-2]. In inorganic-organic hybrid resins, organic polymer components bring good elasticity, tenacity, ductility and low density, while the inorganic components increased hardness, stiffness and resistance to elevated temperature. The prospect of the combination of these two components can create hybrid materials [3]. Our previous studies showed that [3-6] the incorporated inorganic content present in the inorganic-organic hybrid resins significantly influenced the polymerization shrinkage, physico-mechanical properties and biocompatibility of photocured composite, which motivated for the synthesis of novel antimicrobial and thermally stable inorganic-organic hybrid resins. In the present study, we synthesized inorganic-organic hybrid resins containing alkoxides of calcium (CaR1), magnesium (MgR1) and zinc (ZnR1) with polymerisable dimethacrylate groups. The resins were synthesized through modified sol-gel method using 3-trimethoxy silyl propyl methacrylate as the precursor [7]. Alkoxides of calcium, magnesium and zinc were incorporated in the resin due to its reported functions in biomedical applications [8-14]. The effects of inorganic content on antimicrobial properties and thermal stability of CaR1, ZnR1 and MgR1 were evaluated and compared with reported control material (Bis GMA) [4]. The novel resin was found to have antimicrobial properties and good thermal stability.

Experimental section

The inorganic – organic hybrid resins with polymerizable dimethacrylate group were synthesized through a patented [7] modified sol-gel technique. Resins containing mixtures of alkoxides of calcium /magnesium / zinc were synthesized by reacting γ-Trimethoxy silyl propyl methacrylate and deionised water in the molar ratio (1:4). To the stirred mixture added 1 ml 6N NaOH followed by the addition of calcium hydroxide, zinc acetate and magnesium chloride (0.5% weight of silane) and kept stirred for 8 h. During the synthesis of control resin stirring was continued for 8h, after the addition of 1 ml 6N NaOH. The hydrolyzed silane was kept at room temperature overnight for post condensation. The product obtained was then extracted with ether, washed with distilled water, till alkali free and dried. The photocured composites were prepared through a patented procedure [15]. Inorganic-organic hybrid resin (50 parts) diluted with triethylene glycol dimethacrylate (50 parts) was used as the resin matrix along with 0.5% Diphenyl (2, 4, 6trimethylbenzoyl) phosphine oxide as the photoinitiator. 300 phr of silanated quartz and 12% fumed silica were used as filler. Other chemicals used for the preparation of resin mixture were 4(dimethyl amino) phenethyl alcohol, 4-methoxy phenol, phenyl salicylate, 2-hydroxy-4 methoxy benzophenone and 2, 6 di-tert-butyl -4-methyl phenol (which act as inhibitors, activators and uv stabilizers). Thermal stability of the synthesized resins was evaluated using thermogravimetry as per the international standard (ASTME-1131-98) using thermogravimetric analyzer (SDT-2960 TA Instruments Inc, USA,) [16]. The heating rate used was 10°C/min, in nitrogen atmosphere.

The synthesized resins, filler and other additives were masticated in an agate mortar to get a uniform paste. The paste was packed in to a mold and exposed to visible light having the intensity >300mw/cm^2 for 60s on both sides using Prolite (Caulk/Dentsply, US). Antimicrobial properties were evaluated under dynamic conditions as per – ASTM:E 2149 using E.coli ATCC2592 [17].

Results and discussion:

Compared to control (table 1), resin containing alkoxides of calcium, magnesium and zinc showed higher T_0 T_{50} value. It can be seen from table 1 that incorporation of 0.5 % of $Ca(OH)_2$ to control resin increased the onset of decomposition temperature from 356.26°C to 443.79°C. whereas incorporation of 0.5 % of $Zn(CH_3COOH)_2$ and $MgCl_2$ increased the onset of decomposition temperature from 356.26°C to 425.12°C and 420.37°C respectively (table 1). Higher T_0 and T_{50} values were obtained for CaR1 resin (table 1). 50% decomposition was occurred for CaR1 even at 968.71°C. The weight loss observed after T_{50} to 1000 °C (final degradation temperature) for CaR1 (0.48%), ZnR1 (1.36%) and MgR1 (2.17%) resins were negligibly small, leaving carbonaceous char (table 1). Major weight loss upto T_{50} may be due the decomposition of organic components in the resins. The percentage of carbonaceous char at 990 °C was 36.5 and a weight loss of 13.5% after T_{50} value indicates that inorganic content in the synthesized resins had influence in their thermal stability (table 1). Good thermal stability for CaR1, ZnR1 and MgR1 resins indicates effective bonding between the inorganic and organic components within the resin. Thermally stable bisphenol-A glycidyl methacrylate (Bis GMA) had versatile application in the field of dental restoration due to its aesthetics and good physic-mechanical properties. Here we used Bis GMA as the control material for antibacterial studies. The antimicrobial studies showed that ZnR1 exhibit 22.15 % reduction in E.coli ATCC 25922 compared to Bis GMA, CaR1 and MgR1 after 1 hour exposure (table 2).

Sample Code	Inorganic content added	T_0 (°C)	T_{50} (°C)	% residue at 990 °C
Control	Nil	356.26	477.32	36.5
CaR1	$Ca(OH)_2$	443.79	968.71	49.52
ZnR1	$Zn(CH_3COOH)_2$	425.12	589.99	48.64
MgR1	$MgCl_2$	420.37	649.15	47.83

Table 1: Effect of inorganic content on thermal behaviour of various resins (T_0 and T_{50} values).

Samples	Exposure time	Reduction in E.coli ATCC 25922 (%)
Bis GMA	1 hour	0
CaR1	1 hour	0
ZnR1	1 hour	22.15
MgR1	1 hour	0

Table 2: Comparison of antimicrobial study of CaR1, ZnR1 and MgR1 based photocured composites with control Bis GMA based composites using E.coli ATCC 25922 bacteria.

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