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High strength re-mineralizing, antibacterial dental composites with reactive calcium phosphates

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ABSTRACT

Objective. Development of high strength dental composites with adhesive, antibacterial and re-mineralizing potential.

Materials. Urethane and triethylene glycol dimethacrylates were combined with HEMA (10 or 20 wt%) and 2MP (2 or 10 wt%), antibacterial chlorhexidine (2.5 wt%) and chemical cure initiators. Reactive mono/tri calcium phosphate (CP) mixed with silica/silicon carbide nanoparticles (S) (CP:S weight ratio 1:2 or 2:1) was added (50 wt%).

Results. Decreasing CP/S ratio and HEMA content reduced monomer conversion at 15 min from 93 to 63%. Conversely, decreasing CP/S increased initial "dry" compressive (137–203 MPa) and flexural (79–116 MPa) strength. With high HEMA content, these decreased by ~15–20 MPa upon 24 h water storage. With low HEMA content, average decline was <8 MPa due to reduced water sorption. Early water sorption induced mass increase, volume expansion, mono calcium phosphate dissolution and chlorhexidine release, were proportional to the initial calcium phosphate content. Furthermore, they increased ~1.5 fold upon raising HEMA wt%. These diffusion controlled processes and strength decline slowed after 24 h as phosphates reaction bound water within the materials. Increasing 2MP concentration reduced calcium release but did not affect strength. Formulations with high CP/S indicated greater antibacterial activity in agar diffusion and in vitro biofilm tests.

Significance. New material use beneath a conventional composite could potentially reduce high failure rates associated with residual caries and bacterial microleakage.

1. Introduction

Dental caries involves acid-producing bacteria that enhance dissolution of hydroxyapatite from both enamel and dentin. In dentin, remaining collagen is subsequently degraded by matrix metalloproteinase enzymes (MMPs) [1]. In order to arrest disease progression and restore shape and function, damaged dental structures were previously replaced by amalgam but this is increasingly being replaced by more esthetic composite materials [2]. The use of adhesives with dental composites has reduced the need for over cutting and sound

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tooth removal procedures previously adopted to ensure amalgam retention [3]. Rapid bond strength deterioration upon thermal or mechanical cycling, however, is a well known problem [4]. Moreover, composites shrink upon polymerization. The resultant stress can enhance tooth adhesion loss, microgap formation and ultimately bacterial microleakage [5]. This, in combination with lack of antibacterial action, can result in current composite resin restorations having a greater risk of secondary caries and being replaced at a higher rate than amalgam [6–8].

To overcome bacterial microleakage, chlorhexidine (CHX) has previously been added into dental composites [9]. In addition to being antibacterial, this drug can inhibit MMP action [10]. Composites with early release of chlorhexidine might reduce the need for extensive disease affected tissue removal as advocated in modern tooth restoration procedures [11]. Unfortunately, CHX is not readily released from the bulk of a conventional composite. This problem has been overcome through partial replacement of hydrophobic composite monomers with the hydrophilic monomer, hydroxyethylmethacrylate (HEMA). Hyrophilicity enhances water sorption and expansion which counteracts polymerization shrinkage. It also increases early drug release and antibacterial action [9]. Unfortunately, strength is reduced.

An alternative method employed to reduce bacterial microleakage with composite use has been addition of amorphous calcium phosphate. It has been proposed that release of calcium phosphate may help re-mineralization of surrounding dentin [12–14]. Poor initial strength, however, was common due to lack of any bonding mechanism between the filler and matrix phase [15].

Additionally, reactive acidic and basic mono and tri calcium phosphate fillers (MCPM/β-TCP) have been included in dental composites [16]. Use of the hydrophilic and soluble MCPM alone caused rapid water sorption, calcium phosphate release and decline in strength. When β-TCP was added, MCPM in the surface of the material still dissolved. MCPM in the bulk, however, reacted with the β-TCP binding water in brushite (dicalcium phosphate dihydrate) crystals.

MCPM/β-TCP fillers and chlorhexidine were previously incorporated in urethane (UDMA)/triethylene glycol (TEGDMA)/hydroxyethyl (HEMA) di and mono methacrylate resins [16]. The combined presence of high levels of hydrophilic MCPM (25–38 wt% of composite) and HEMA (50 wt% of resin) enabled much higher CHX release than generally possible with dental composites [9]. It also, however, caused excessive water sorption, swelling and early strength decline.

The following new study aim is to address if reduction in HEMA level (10–20 wt%) can control these reactive filler composite problems without overly inhibiting release of chlorhexidine. Furthermore, the reactive calcium phosphate fillers are partially replaced with silica/silicon carbide particles in an attempt to improve early strengths whilst maintaining some calcium phosphate release. Additionally, the calcium binding monomer (Bis[2-(methacryloyloxy)ethyl] phosphate (2MP)) is added to assess if this can provide a bonding mechanism between the calcium phosphate fillers and monomer, thereby raising strength.

2. Materials and methods

2.1. Sample preparation

2.1.1. Filler

β-TCP (β-tricalcium phosphate) (Fluka, Germany) of particle diameter < 15 μm was used without modification. MCPM (monocalcium phosphate monohydrate) (Fluka, Germany) particles were ground by means of a ball mill. To obtain MCPM particles of 20–38 μm diameter (median 29 μm), the ground powder was sieved through Endecotts sieves (Laboratory Sieve, UK).

Silica nanoparticles (Sigma–Aldrich, UK) (diameter 10–20 nm) were mixed with an equal mass of silicon carbide nanoparticles (Sigma–Aldrich, UK) (diameter < 100 nm). Mixing was undertaken in ethanol (BDH, UK) using a magnetic stirrer bar and hot plate (Heidolph Stirrer, UK). Samples were stirred in a fume hood until dry. The dried mixture was subsequently heated in an oven (Lenton Thermal Design Ltd., UK) at 800 °C for 30 min. After cooling, the silica–silicon carbide was reacted with 4% 3-methacryloxypropyltrimethoxysilane (MPS) (Aldrich–Sigma, UK) by stirring for 1 h at room temperature in ethanol. The silanized mixture was subsequently allowed to dry for 1 h at room temperature and then at 37 °C for 24 h. Using a ball mill, the silanized nano-silica–silicon carbide powder was finally ground to obtain particles in the range 20–38 μm.

2.1.2. Accelerator and initiator containing pastes

The composite resin consisted of UDMA (Rhom, Germany) base monomer: TEGDMA diluent (Sigma–Aldrich, UK) (1:1 weight ratio). This provided fluid monomers that could readily mix with other components and cure well with chemical initiators. HEMA (Sigma–Aldrich, UK) was added at 10 or 20 wt% as previous work suggests this should provide measurably different but not excessive levels of water sorption [9,16]. Bis[2-(methacryloyloxy)ethyl] phosphate (2MP) (Polyscience, USA) was added at lower levels (2 or 10 wt% of resin). These levels would be sufficient to provide a thin surface layer around any calcium phosphate particles without monomer phase separation. Chlorhexidine diacetate (Sigma–Aldrich, UK) was fixed at 2.5 wt% of the resin. This ensured most of the chlorhexidine was dissolved in the monomer phase but release was sufficient for ready quantification by UV. Either N,N-dimethyl-p-toluidine accelerator (DMPT) (Sigma–Aldrich, UK) (1 wt%) or benzoyl peroxide (BP) initiator (Sigma–Aldrich, UK) (2 wt%) with 2,6-di-tert-butyl-4-methyl phenol inhibitor (BMP) (Fluka, Spain) (0.05 wt%) was subsequently included. Preliminary investigations indicated this gave stable liquids that could cure in a short period after mixing.

Filler was added at a level of 50 wt% of the total mass to produce separate initiator and activator pastes. 50 wt% was the maximum filler loading that gave pastes of reasonable consistency. The filler consisted of MCPM and β-TCP (CP) in equal masses combined with silica–silicon carbide particles (S). CP:S weight ratio was 2:1 or 1:2. Preliminary calculations and earlier work [16] suggested these levels should help ensure sufficient water sorption to balance polymerization shrinkage.