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Ion-releasing dental restorative composites containing functionalized brushite nanoparticles for improved mechanical strength

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ARTICLE INFO

Article history:

Received 11 May 2017

Received in revised form

6 August 2017

Accepted 19 January 2018

Keywords:

Dental composite

Brushite

Nanoparticle synthesis

Flexural strength

Ion release

ABSTRACT

Objectives. This study describes the synthesis of brushite nanoparticles ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) functionalized with triethylene glycol dimethacrylate (TEGDMA) and their application in dental restorative composites with remineralizing capabilities.

Methods. Nanoparticles were synthesized, with TEGDMA being added to one of the precursor solutions at three different molar ratios (0:1, 0.5:1 and 1:1, in relation to the ammonium phosphate precursor). Then, they were added (10 vol%) to a photocurable dimethacrylate matrix containing 50 vol% of reinforcing glass particles. The resulting composites were tested for degree of conversion, biaxial flexural strength and elastic modulus (after 24 h and 28 days in water), and ion release (over a 28-day period). Commercial composites (one microhybrid and one microfilled) were tested as controls.

Results. The final TEGDMA content in the functionalizing layer was modulated by the molar ratio added to the precursor solution. Functionalization reduced nanoparticle size, but did not reduce agglomeration. Improved mechanical properties were found for the composite containing nanoparticles with higher TEGDMA level in comparison to the composite containing non-functionalized nanoparticles or those with a low TEGDMA level. All brushite composites presented statistically significant reductions in strength after 28 days in water, but only the material with high-TEGDMA nanoparticles retained strength similar to the microhybrid commercial control. Overall, ion release was not affected by functionalization and presented steady levels for 28 days.

Significance. Though agglomeration was not reduced by functionalization, the improvement in the matrix-nanoparticle interface allowed for a stronger material, without compromising its remineralizing potential.

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<https://doi.org/10.1016/j.dental.2018.01.026>

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1. Introduction

Remineralization of caries-like artificial lesions by resin composites containing calcium orthophosphate (CaP) nanoparticles has been demonstrated *in vitro* [1–5]. Also, the protective effect of these materials against enamel demineralization in the presence of cariogenic biofilm was shown *in situ* [6]. Unfortunately, the incorporation of CaP particles in the composite leads to significant reductions in their fracture strength and fracture toughness due to lack of chemical interaction with the resin matrix [7–10]. Also, the nanoparticles tend to cluster and form micron-size agglomerates with low cohesive strength that do not represent an obstacle to crack propagation within the material [7]. Therefore, the fraction of these bioactive fillers in the composite should be kept to a minimum, assuring that ion release will be enough to foster remineralization, and must be combined with reinforcing fillers, such as whiskers [11,12] or silanated glass particles [13–15].

Additional strategies were also tested to minimize the strength loss in CaP composites. For example, functionalization of CaP particles with methacryloxypropyl trimethoxysilane (MPTMS) was successful in improving composite strength; however, silanes are hydrophobic, hindering the access of water to the particle and significantly reducing ion release [16,17]. Recently, brushite nanoparticles ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, dicalcium phosphate dihydrate) functionalized with triethylene glycol dimethacrylate (TEGDMA, Fig. 1) were synthesized [18]. When added to one of the precursor solutions, TEGDMA would be capable of binding to the calcium ions of the growing crystals through ion-dipole bonds with the oxygen atoms in the ethylene glycol groups ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$). The TEGDMA in the functionalized layer can co-polymerize with other dimethacrylate monomers in the resin matrix, increasing particle-matrix interaction. The validity of this approach was confirmed by a 32% increase in flexural strength of a BisGMA/TEGDMA material containing 20 vol% of functionalized nanoparticles, in comparison with a material containing non-functionalized nanoparticles. Moreover, due to the relatively hydrophilic nature of TEGDMA, particle functionalization did not impair ion release [19].

The incorporation of organic compounds in the synthesis of CaP nanoparticles may lead to changes in some of their characteristics, such as their size, surface area and agglomeration [20]. These aspects, along with the amount of functionalizing agent around the particles are important parameters for the quality of the particle-matrix interface and, consequently, for the composite mechanical and ion-releasing behaviors. Furthermore, the contribution of TEGDMA-functionalized brushite nanoparticles for the mechanical properties of composites seems to be dependent upon the particle fraction in the material and aging conditions. For example, while nanoparticle functionalization increased the initial strength of composites containing both 10 vol% and 20 vol% of nanoparticles in comparison to the control containing non-functionalized nanoparticles, after 28 days in water only the composites with the 10% particle fraction were stronger than the control [21].

The focus of the present study was on the effect of the amount of TEGDMA in the functionalizing layer on composite

mechanical properties and ion release. Brushite nanoparticles were synthesized with different TEGDMA concentrations and experimental composites containing these nanoparticles were tested against suitable controls, including two commercial composites. The objectives were: (1) evaluate the effect of different TEGDMA concentrations on the characteristics of the brushite nanoparticles and (2) to test the null hypothesis that DCPD functionalization does not affect composite mechanical properties and ion release.

2. Materials and methods

2.1. Synthesis and characterization of TEGDMA-functionalized brushite nanoparticles

Brushite nanoparticles were synthesized via sol-gel process by the stoichiometric reaction between calcium nitrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (all chemicals from Sigma-Aldrich, St. Louis, MO, USA), and dibasic ammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$ [18]. TEGDMA (2-methyl-2-propenoic acid) was added to the ammonium phosphate solution (0.08 M) in molar ratios (TEGDMA: $(\text{NH}_4)_2\text{HPO}_4$) of 0.5 or 1.0. The calcium nitrate solution (0.08 M) was added drop-wise (9 mL/min) to the ammonium phosphate solution under constant stirring. After that, the suspension was kept under stirring for 24 h followed by a 30-min decantation period. The precipitate was rinsed in water and vacuum-filtered, and the resulting gel was freeze-dried. Besides the two functionalized nanoparticles, a third synthesis was performed without the incorporation of TEGDMA to the ammonium phosphate solution. These non-functionalized nanoparticles (NF) were used as control.

The calcium orthophosphate phase constituting the nanoparticles was determined by X-ray diffraction (Multi-flex, Rigaku Corp., Tokyo, Japan). TEGDMA content (percentage by weight) in the functionalized particles was calculated based on carbon mass fractions obtained by CHN (carbon-hydrogen-nitrogen) analysis (Perkin-Elmer Model 240 Elemental Analyzer, Waltham, MA, USA). The nanoparticles true density was determined in a helium pycnometer (Ultra-pyc 1200e, Quantachrome Instruments, Boynton Beach, FL, USA). Surface area was calculated based on nitrogen adsorption isotherms using the BET (Brunauer, Emmet and Teller) method [22] (Nova 1200e, Quantachrome Instruments). Prior to this analysis, the functionalized nanoparticles were subjected to five sonication cycles in acetone to remove as much of the TEGDMA as possible and allow for determination the surface area of the brushite core.

Size distribution of the nanoparticles agglomerates was determined by laser scattering (Mastersizer 2000, Malvern Instruments Ltd., Worcestershire, UK). Nanoparticles were observed under TEM (transmission electron microscopy, JEM model 1010, Tokyo, Japan) and the length of their long axis was measured ($n=70$) using the Image J software (National Institute of Health, Bethesda, MD, USA).

2.2. Composites preparation

Bisphenol A glycidyl dimethacrylate (BisGMA) and TEGDMA were mixed in equimolar proportion, along with cam-

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