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# Bioactive composites containing TEGDMA-functionalized calcium phosphate particles: Degree of conversion, fracture strength and ion release evaluation

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ABSTRACT

*Objective.* To evaluate the strength and ion release of experimental composites containing TEGDMA-functionalized calcium phosphate particles.

*Methods.* Seven composites containing equal parts (in mols) of BisGMA and TEGDMA and 60 vol% of fillers were manipulated. Filler phase was constituted by silanized barium glass and 0% (control), 10% or 20% (volume) of dicalcium phosphate dihydrate (DPCD) particles, either non-functionalized or functionalized with two different TEDGMA contents. DCPD particles were synthesized and characterized by X-ray diffraction (XRD), elemental analysis, surface area and dynamic light scattering. Composites were tested for degree of conversion (DC) by near-FTIR. Biaxial flexural strength (BFS) was determined after 24 h and 28 days in water. Calcium and phosphate release after 7 days was assessed using inductively coupled plasma optical emission spectrometry (ICP-OES). Data were analyzed by ANOVA/Tukey test (alpha:5%).

*Results.* XRD confirmed the crystalline structure corresponding to DCPD. Elemental analysis revealed particles with zero, 14% or 22% TEGDMA, with similar $D_{50}$ (around 19 μm) and surface areas from 3.5 to 11.4 $m^2/g$. The presence of DCPD did not reduce DC. After 24 h, functionalization (both 14% and 22% TEGDMA) improved composite strength in comparison to non-functionalized DCPD, both at 10% and 20% levels. After 28 days, BFS of materials containing 10% functionalized DCPD were statistically similar to the control containing only barium glass. Among composites containing 10% DCPD, particle functionalization with 14% TEGDMA did not jeopardize ion release.

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*Significance.* At 10 vol%, the use of TEGDMA-functionalized CaP particles improved composite strength in relation to non-functionalized particles, while maintaining similar ion release levels.



## 1. Introduction

Over the years, the incorporation of calcium orthophosphates [1–4] and bioactive glass particles [5,6] in resin-based materials has been studied as a possible path to promote tooth remineralization and reduce the risk of secondary caries at the tooth/restoration interface [1,7–10]. These particles behave as ion sources, releasing calcium and phosphate to the surrounding medium and creating a supersaturated environment that favors mineral deposition on the tooth.

Unfortunately, the addition of CaP particles to unfilled resins significantly lowers their strength [11,12]. This impaired mechanical behavior is ascribed to the lack of a strong chemical bond between the bioactive particles and the resin phase, as well as the low cohesive strength of the CaP agglomerate itself [11–13]. Several approaches have been tested to increase the mechanical properties of bioactive composites. For example, an experimental composite containing hydroxyapatite particles functionalized with acrylic acid showed a significantly higher flexural strength in comparison with a control material containing unmodified CaP particles [14]. Silanization of CaP particles was also tested and, though composite strength increased in comparison to the use of non-silanized particles, ion release was negatively affected [15,16].

The association between reinforcing fillers and bioactive particles seems to offset some of the negative effect of the latter on composite mechanical properties. For example, when 40 wt% of tetracalcium phosphate (TTCP) was added to an unfilled resin, 20 wt% of silanated glass had to be added in order to recover the flexural strength of the unfilled resin [12]. In another study, the addition of 10 wt% reinforcing fillers to an experimental material containing 40 wt% amorphous calcium phosphate (ACP) also contributed to improve composite strength, with no adverse effect on ion release [17].

Recently, DCPD nanoparticles functionalized with triethylene glycol dimethacrylate (TEGDMA) were synthesized [18]. Among the different calcium orthophosphate phases, dicalcium phosphate dihydrate (DCPD, $CaHPO_4.2H_2O$) presents a relatively high solubility [19], which makes it more suitable as ion source than less soluble phases, such as hydroxyapatite (HA). Also, its refractive index (1.54–1.55) [20] is similar to barium glass (1.53) [21]. HA, for example, has a refractive index of 1.63–1.67, which compromises light transmission during photoactivation, as well as esthetics [14]. By adding the monomer to one of the reacting solutions (*i.e.*, prior to DCPD crystallization), it would attach to the $Ca^{2+}$ at the nanoparticle surface at early stages of its growth, when reactivity is at its maximum. Also, the TEGDMA in the functionalizing layer would co-polymerize with monomers of the resin matrix, increasing the compatibility between the nanostructured agglomerates and the resin. Preliminary studies showed that the incorporation of TEGDMA-functionalized DCPD in a BisGMA:TEGDMA resin matrix increased biaxial flexural strength by 32% in comparison with a material containing non-functionalized particles.

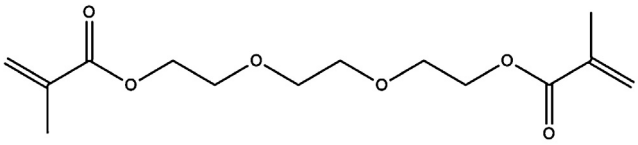

**Fig. 1 – Structural formula of triethylene glycol dimethacrylate (TEGDMA) used as functionalizing agent.**

This investigation is a follow-up from a previous study where the substitution of silanized barium glass with proprietary, non-functionalized DCPD nano-structured agglomerates in experimental composites resulted in up to 35% reduction in fracture strength [13]. In the present investigation, TEGDMA-functionalized DCPD particles were tested partially replacing the reinforcing fillers. The ultimate goal was to determine if the use of functionalized DCPD particles would improve composite strength (in comparison to the material containing non-functionalized particles) without jeopardizing ion release. Additionally, the effect of the amount of TEGDMA in the functionalizing layer was also verified. The null hypotheses were: (1) replacing 10 vol% or 20 vol% of silanized glass fillers by DCPD particles does not affect composite degree of conversion and strength (prior and after aging in water for 28 days), regardless of the DCPD content or the presence of a TEGDMA functionalizing layer, (2) ion release is not affected by DCPD content or by functionalization of the DCPD particles.

## 2. Methods

### 2.1. *Synthesis and characterization of dicalcium phosphate dihydrate (DCPD) nanoparticles*

DCPD ($CaHPO_4.2H_2O$) nanoparticles were synthesized through the reaction between ammonium phosphate $(NH_4)_2HPO_4$, and calcium nitrate $Ca(NO_3)_2.4H_2O$ (both from Sigma–Aldrich Co., St. Louis, MO, USA) by a sol–gel process [18]. Equimolar solutions (0.078 mol/L) were prepared with deionized water at room temperature and mixed with a magnetic stirrer. The ammonium phosphate solution received 6.86 g (0.024 mol) of triethylene glycol dimethacrylate (Fig. 1, TEGDMA, Mw = 286 g/mol, Sigma–Aldrich). 400 mL of the calcium nitrate solution was added to the same volume of the ammonium phosphate/TEGDMA solution using a peristaltic pump (9 mL/min). The resulting mixture was kept under stir-