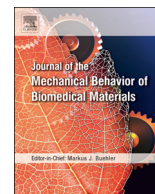




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## Mechanical characterization and ion release of bioactive dental composites containing calcium phosphate particles

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### A B S T R A C T

**Objective:** to verify the effect of the addition of dicalcium phosphate dihydrate (DCPD) particles functionalized with di- or triethylene glycol dimethacrylate (DEGDMA or TEGDMA) on the degree of conversion (DC), post-gel shrinkage (PS), mechanical properties, and ion release of experimental composites.

**Methods:** Four composites were prepared containing a BisGMA/TEGDMA matrix and 60 vol% of fillers. The positive control contained only barium glass fillers, while in the other composites 15 vol% of the barium was replaced by DCPD. Besides the functionalized particles, non-functionalized DCPD was also tested. DC after 24 h (n = 3) was determined by FTIR spectroscopy. The strain gage method was used to obtain PS 5 min after photoactivation (n = 5). Flexural strength and modulus (n = 10) were calculated based on the biaxial flexural test results, after specimen storage for 24 h or 60 days in water. The same storage times were used for fracture toughness testing (FT, n = 10). Calcium and phosphate release up to 60 days was quantified by ICP-OES (n = 3). Data were analyzed by ANOVA/Tukey test (alpha: 5%).

**Results:** Composites containing functionalized DCPD presented higher DC than the control (p < 0.001). The material containing DEGDMA-functionalized particles showed higher PS than the other composites (p < 0.001). After 60 days, only the composite with DEGDMA-functionalized DCPD presented fracture strength similar to the control, while for flexural modulus only the composite with TEGDMA-functionalized particles was lower than the control (p < 0.001). FT of all composites containing DCPD was higher than the control after 60 days (p < 0.005). Calcium release was higher for the composite with non-functionalized DCPD at 15 days and no significant reductions were observed for composites with functionalized DCPD during the observation period (p < 0.001). For all the tested composites, phosphate release was higher at 15 days than in the subsequent periods, and no difference among them was recorded at 45 and 60 days (p < 0.001).

**Conclusions:** DCPD functionalization affected all the studied variables. The composite with DEGDMA-functionalized particles was the only material with strength similar to the control after 60 days in water; however, it also presented the highest shrinkage. The presence of DCPD improved FT, regardless of functionalization. DCPD functionalization reduced ion release only during the first 15 days.

### 1. Introduction

Resin-based composites containing calcium orthophosphate particles (CaP) are able to foster remineralization of enamel caries-like lesions *in vitro* (Langhorst et al., 2009), as well as inhibit the development of new lesions *in situ* (Melo et al., 2013a). Also, they have been tested as orthodontic cements (Liu et al., 2018), in atraumatic restorative treatment (ART) (Peters et al., 2010) and dentin bonding systems (Melo et al., 2013b). Unfortunately, the mechanical properties of these

bioactive materials are usually lower than those presented by conventional composites due to the poor interaction between the CaP particles and the resin matrix, which make them behave as stress raisers and facilitate crack propagation within the composite (Xu and Moreau, 2010; Chiari et al., 2015).

The synthesis of dicalcium phosphate dihydrate particles (DCPD) functionalized with triethylene glycol dimethacrylate (TEGDMA) was described as a new strategy to improve their interfacial strength with the resin phase (Rodrigues et al., 2014). TEGDMA is a monomer

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ubiquitously found in commercial resin composite formulations and when added to one of the ion precursor solutions (*ab initio* functionalization) can establish ion-dipole bonds with calcium ions in the growing DCPD crystals via ethylene glycol groups (-O-CH<sub>2</sub>-CH<sub>2</sub>-) (Yoshida and Kihara, 1987; Morra, 1993). Additionally, functionalization would improve the wetting of the particles by the resin phase, contributing for a better mechanical interlocking. In fact, a dimethacrylate-based material containing TEGDMA-functionalized DCPD particles presented 32% higher fracture strength in comparison to a material containing non-functionalized particles (Rodrigues et al., 2016a).

The final TEGDMA content on the particle can be modulated by varying the amount of monomer added in the synthesis. Though higher TEGDMA contents improve the composite mechanical behavior (Rodrigues et al., 2018), it may affect other properties as well. For instance, composites containing DCPD particles with TEGDMA mass fractions higher than 14% (determined by elemental analysis) showed higher degree of conversion than the material containing non-functionalized particles. The molecular mobility of TEGDMA granted by its ether linkages increases the probability of polymer chain growth and, though this mobility is probably reduced by the fact these monomers are attached to the DCPD surface, the TEGDMA-rich domains created around the DCPD cores seem to contribute for the material's overall conversion (Alania et al., 2016). Considering the linear relationship between degree of conversion and polymerization shrinkage (Shah and Stansbury, 2014), it is possible that the use of TEGDMA-functionalized DCPD could result in an undesirable increase composite polymerization stress, jeopardizing the integrity of the tooth/restoration interface (Braga et al., 2005).

Functionalization of DCPD particles with other ethylene glycol dimethacrylate (EGDMA) derivatives resulted in particles with different surface areas and size distribution, depending on the length of the spacer group (*i.e.*, number of ethylene glycol groups) (Natale et al., 2018). When added to one of the precursor solutions, ethylene glycol derivatives act as co-solvents, changing the surface tension of the reaction medium. That, in turn, affects crystal nucleation and, consequently, the characteristics of the final particle (Rodrigues et al., 2018). As an example, particles functionalized with diethylene glycol dimethacrylate (DEGDMA) showed the highest monomer content and surface area, and the lowest median particle size in relation to non-functionalized DCPD or those functionalized with EGDMA, TEGDMA or TETDMA (tetraethylene glycol dimethacrylate). Therefore, it is important to verify the effect of these DEGDMA-functionalized DCPD particles on the mechanical properties and polymerization shrinkage of experimental composites.

The effectiveness of remineralizing restorative materials relies upon a long-term sustained ion release. Unfortunately, most of the information available followed ion release for relatively short periods of time, usually 28 days or less (Xu and Moreau, 2010; Chiari et al., 2015; Alania et al., 2016; Marovic et al., 2014a; Xu et al., 2009; Skrtic et al., 1996). Still, it is possible to find studies that verified the occurrence of ion release in longer periods, of 56 days (Xu et al., 2007, 2010) and 70 days (L. Zhang et al., 2016). As ion release implies in particle surface dissolution, in theory, this long-term release could increase the water

pathways through the particle-matrix interface, compromising the stability of CaP-containing composites.

Composite degradation is related to the presence of ester groups (-COO-) in the monomers structures, subjected to oxidation and hydrolysis when in contact with saliva and other fluids (Santerre et al., 2001). Matrix and resin-particle interfacial degradation reduce the composite elastic modulus (Ferracane et al., 1995), flexural strength (Arikawa et al., 1995; Drummond and Miescke, 1991) and fracture toughness (Ferracane et al., 1995; Truong and Tyas, 1988). Very few studies evaluated the degradation of CaP-containing composites. Materials containing 10% or 20% (by mass) of amorphous calcium phosphate (ACP) in a total inorganic content of 75% (ACP + reinforcing glass) did not differ from the control in terms of fracture strength after two years in water (Moreau et al., 2012). On the other hand, composites containing 10% or 20% (by volume) of non-functionalized DCPD and a total inorganic content of 60 vol% presented more severe reductions in flexural strength, flexural modulus, and fracture toughness after 28 days in water in relation to the control (without DCPD) (Chiari et al., 2015).

Based on the above, the present study aimed at evaluating the behavior of experimental composites containing functionalized DCPD particles in terms of mechanical properties, volumetric shrinkage, degree of conversion and 60-day ion release. Material degradation was indirectly accessed by the comparison of mechanical properties determined after 24 h and 60 days in water. The working hypotheses were (1) composite mechanical properties (namely, biaxial flexural strength, flexural modulus and fracture toughness) would improve with the use of functionalized DCPD particles in comparison to non-functionalized DCPD, (2) the presence of DCPD (functionalized or not) would not increase composite degradation after prolonged water storage 2) the higher in overall organic content in composites containing functionalized DCPD would increase degree of conversion and volumetric shrinkage in relation to the control and the composite with non-functionalized DCPD and 3) DCPD functionalization would not interfere with ion release from the composite.

## 2. Material and methods

### 2.1. Composite formulation

The resin phase of the experimental composites consisted of a BisGMA/TEGDMA mixture (1:1 in mols, all chemicals from Sigma Aldrich, St Louis MI, USA), plus camphorquinone and 2-(dimethylaminoethyl) methacrylate (0.5% by mass each) as photoinitiators. Four different composites were prepared, all of them with a total of 60% by volume of filler particles. Three of them contained 15 vol% of DCPD particles (functionalized with DEGDMA or TEGDMA, or non-functionalized) and 45 vol% of silanized barium glass (2 μm), while the control contained only barium glass particles. The synthesis of the DCPD particles are described in details elsewhere (Rodrigues et al., 2014). Briefly, a calcium nitrate solution (0.2 mol L<sup>-1</sup>) was added drop-wise to an ammonium dihydrogen phosphate solution (0.2 mol L<sup>-1</sup>) and kept under stirring for 24 h. Functionalization was achieved by adding the

**Table 1**  
Characteristics of the dicalcium phosphate dihydrate particles used in the study.

	Organic content (wt%) <sup>a</sup>	Density (g/cm <sup>3</sup> ) <sup>b</sup>	Surface area (m <sup>2</sup> /g) <sup>c</sup>	Equivalent spherical diameter (D <sub>50</sub> , in μm, D <sub>10</sub> -D <sub>90</sub> in parentheses) <sup>d</sup>
Non-functionalized DCPD (NF)	N/A	2.4	28	25 (13–50)
DEGDMA-functionalized DCPD (DG)	34.4	1.7	40	12 (6–23)
TEGDMA-functionalized DCPD (TG)	14.1	2.2	16	19 (10–37)

<sup>a</sup> Determined by elemental analysis.

<sup>b</sup> Determined by helium picnometry.

<sup>c</sup> Calculated based on nitrogen adsorption isotherms using the BET (Brunauer, Emmet and Teller).

<sup>d</sup> determined by dynamic laser scattering. For details on the characterization methods, please refer to (Natale et al., 2018).

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