





Mechanical properties and surface roughness of polymer-based materials containing DCPD particles

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Abstract: The purpose of this study was to synthesize dicalcium phosphate dihydrate (DCPD) particles functionalized with triethylene glycol dimethacrylate (TEGDMA) through different routes by varying the receptor solution: ammonium phosphate (AP groups) or calcium nitrate (CN groups) and the moment in which TEGDMA was incorporated: *ab initio* (ab) or at the end of dripping the solution (ap). Two syntheses were performed without adding TEGDMA (nf). The particles were characterized by X-ray diffractometry, true density (using a helium pycnometer), surface area, and scanning electron microscopy. A 20 vol% of DCPD particles from the D, E, and F groups was added to the resin matrix to determine the degree of conversion (DC), biaxial flexural strength (BFS), the flexural modulus (FM), and surface roughness after an abrasive challenge (RA). A group with silanized barium glass particles was tested as a control. The data were submitted to ANOVA/Tukey's test (DC, BFS, and RA), and the Kruskal-Wallis test (FM) ($\alpha = 0.05$). BFS values varied between 83 and 142 MPa, and the CN_ab group presented a similar value (123 MPa) to the control group. FM values varied between 3.6 and 8.7 GPa (CN_ab and CN_nf groups, respectively), with a significant difference found only between these groups. RA did not result in significant differences. The use of calcium nitrate solution as a receptor, together with *ab initio* functionalization formed particles with larger surface areas. Higher BFS values were observed for the material containing DCPD particles with a higher surface area. In general, the DC, FM, and RA values were not affected by the variables studied.

Keywords: Calcium Phosphates; Composite Resins; Flexural Strength.

Introduction

Restorative materials are inert, biocompatible, and mechanically resistant. However, new development strategies are focusing efforts on regenerative restorative biomaterials¹ capable of reversing the progression of caries lesions due to increasingly prioritized minimal intervention.^{2,3,4}

The incorporation of particles consisting of different phases of calcium orthophosphates (CaP) in resinous matrices, such as dicalcium phosphate dihydrate (DCPD), amorphous calcium phosphate (ACP), and tetracalcium phosphate (TTCP), are capable of releasing calcium and hydrogen

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phosphate ions into the surroundings.^{5,6,7} Resin composites containing CaP particles remineralize enamel and dentin.^{4,7} A significant reduction in dental enamel demineralization has been observed *in situ* when using composite containing ACP particles.³ Finally, these materials promote mineral recovery of enamel–dentin affected by caries *in vivo*.⁸

Unlike barium and silica glass particles commonly found in commercial materials, calcium phosphate particles do not act as strengtheners of restorative material.⁹ In contrast, the absence of a strong chemical interaction between the calcium phosphate particles and the polymer causes these particles to behave as large defects in the material,¹⁰ causing stress and creating potential sites for crack initiation.^{9,11} In fact, incorporating 20% mass of TTCP particles into a resin matrix causes a 50% reduction in strength.¹² The strength of a material containing 20 vol% DCPD particles corresponds to less than half of the observed values for a silanized silica-containing composite.¹³ Thus, one of the main challenges moving forward with applications of these materials in clinical practice is to reconcile ion release with satisfactory mechanical properties.^{2,11}

One of the alternatives proposed to increase the compatibility of these particles with the resin matrices is particle surface functionalization.^{14,15} Calcium phosphate particles, such as DCPD, are synthesized through very simple routes and can be functionalized at different times. Functionalization concomitant to particle precipitation (*ab initio*) was proposed with the objective of providing a chemical interaction with the resinous monomers and to reduce particle size.^{6,16,17} DCPD particles functionalized *ab initio* with the triethylene glycol dimethacrylate monomer (TEGDMA) forms higher surface area particles.¹⁷ In addition, up to a 40% increase in fracture strength values is observed when resinous materials containing functionalized DCPD particles were compared to materials with nonfunctionalized particles.^{6,13,18} DCPD functionalization after complete precipitation of particles has not been evaluated.

During coprecipitation synthesis of DCPD particles, the calcium nitrate solution is dripped onto an ammonium phosphate (AP) solution containing the

functionalizing monomer.^{6,11,17,19} Switching the receptor solution may also lead to changes in particle size and morphology. Therefore, the aim of this study was to evaluate the effects of different routes of synthesis through coprecipitation, alternating the receptor solution and the moment of functionalization (*ab initio* or after particle precipitation) on the characteristics of DCPD particles. DCPD particles were added to resin matrices to analyze the degree of conversion (DC), mechanical properties, and surface roughness of the materials.

Methodology

Synthesis and characterization of the particles

DCPD particles were synthesized from solutions of ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) and calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Sigma-Aldrich Brazil Ltd.®, São Paulo, Brazil), both at a concentration of 0.2 mol/L. For particles functionalization, triethylene glycol dimethacrylate monomer (TEGDMA) was used at a molar ratio of 1:1 in relation to the ammonium phosphate solution. The experimental groups were defined by varying the recipient solution: ammonium phosphate solution (AP groups) and calcium nitrate solution (CN groups). The moment the functionalized monomer was incorporated was also a factor in the study; either added to the receiver solution before dripping (*ab initio*: ab groups) or at the end of the precipitation of the particles (after precipitation: ap groups). Two additional syntheses were performed without adding TEGDMA as controls (nonfunctionalized: nf groups). The suspensions were shaken for 3 hours and the by-products as well as the excess TEGDMA (when added to the synthesis) were removed by rinsing and vacuum filtration. The final products were frozen and lyophilized to a white powder.

The particles were characterized by X-ray diffraction (XRD) with readings between 10° and 60°, geometry $q/2q$, using nickel-filtered $\text{CuK}\alpha$ radiation of 40 kV and 30 mA (Rigaku-Multiflex, Tokyo, Japan). The percentage of monomer in the functionalized particles was determined indirectly by analyzing real density using a helium pycnometer

(Ultracyc 1200e, Quantachrome Instruments, Boynton Beach, USA). The surface area of the particles was evaluated using adsorption isotherms and the Brunauer–Emmett–Teller (BET) method with the aid of NOVWin software (Quantachrome Instruments, Boynton Beach, USA). Particle morphology was observed under a scanning electron microscope (Quanta FEG600, Eindhoven, The Netherlands). A minimum of 25 particles from each group was measured using Image J software (National Institutes of Health, Bethesda, USA).

Incorporation of the particles in the resinous material

Manipulation of experimental materials

An organic matrix based on BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane, Sigma-Aldrich Co., St. Louis, USA) and TEGDMA (2-methyl-2-propenoic acid, Sigma-Aldrich) in proportions of 1:1 (in mol). DMAEMA photo initiator (Sigma-Aldrich) and camphorquinone (Sigma-Aldrich, Steinheim, Germany) were added in 0.5% of weight; 20% of the volume of the DCPD particles was added to this matrix. Particles with the highest surface area in the previous section of the study were chosen for this evaluation. Resinous material containing 20% of the volume of silanized barium glass particles (0.5 µm) was used as a control.

Degree of conversion

The DC of the resin-based materials was determined by Fourier-transformed infrared spectroscopy (FTIR).²⁰ Disk-shaped specimens were prepared (n = 3; 7 mm × 0.9 mm). The spectrum of the unpolymerized material was obtained in the wavelength range of 4,000–9,840 cm⁻¹ with a resolution of 6 cm⁻¹ (Vertex 70, Bruker Optik GmbH, Ettlingen, Germany). A new spectrum was obtained after 24 hours of photopolymerization, with an energy density of 48 J/cm² (1,200 mW/cm² × 40 s) and storage at 37°C. The area under the vinyl bond absorption band located at 6,165 cm⁻¹ was calculated with Opus v.6 software (Bruker Optics). The DC of the materials was obtained as the ratio of the absorption bands corresponding to carbon:

$$DC = \left(1 - \frac{\text{polymerized}}{\text{unpolymerized}} \right) \cdot 100$$

Biaxial flexural strength and modulus

Disk-shaped specimens (n = 10; 12 × 1.2 mm) were made using a split stainless steel matrix. The materials were inserted at one time and were photopolymerized for 40 s (10 s per quadrant). After 7 days of storage at 37°C, the specimens were fractured in a universal test machine (model 5565, Instron Corp., Canton, USA) using the “piston-on-three-balls” accessory, at a loading rate of 0.5 mm/min. The biaxial flexural strength (BFS) was calculated in MPa using the equations:

$$\sigma_{BI} = \frac{-0,2387P (X - Y)}{b^2}$$

$$X = (1 + \nu) \ln \left(\frac{r^2}{r^3} \right) + \left[\left(\frac{1 - \nu}{2} \right) \right] \left(\frac{r^2}{r^3} \right)^2$$

$$Y = (1 + \nu) \left[1 + \ln \left(\frac{r_1}{r_3} \right) \right] + (1 - \nu) \left(\frac{r_1}{r_3} \right)^2$$

Where P is the maximum fracture load (in N); b is thickness of the disk (in mm); ν is the Poisson coefficient; r₁ is the radius of the circle on which the steel balls (5.0 mm) are positioned; r₂ is the radius of the tip of the piston or the area of load application (0.6 mm); r₃ is the radius of the disk (in mm). The Poisson coefficient adopted was 0.30 for all materials.²¹ The flexural modulus (FM) was calculated using the following equation:

$$E = \frac{\beta P a^2}{\omega h^3}$$

Where E is the FM (in GPa), β is a constant related to disk deflection in the central region (0.509), P is the applied load (in N), a is the radius of the disk (in mm), ω is the deflection at the center, and h is disk thickness (in mm).

Abrasive cycles and profilometry analysis

For each experimental group, cylindrical specimens (n = 10; 4 × 5 mm) were prepared and photopolymerized for 40 s (1,200 mW/cm²) and kept

in an oven at 37°C for 7 days. The specimens were embedded in acrylic resin and then flattened with abrasive Al₂O₃ disks with grades of 220-, 400-, 600-, 1,200-, and 2,000- in polystyrene (Teclago, Vargem Grande Paulista, Brazil) and polished with a felt disk and diamond paste. A surface analysis was performed using an optical profilometer (Proscan 2000, Scantron, Venture Way, Tauton, UK) in a 2 mm length and 1 mm width of the surface of the specimens.

The edges of the test specimens were protected with UPVC (Graphic Tape, Chartpak, Leeds, USA) tape exposing an area corresponding to 1 mm in length in the center of the test specimens under analysis. The protected areas were used as the point of reference in the study after the abrasive challenge. The specimens were introduced into an automatic toothbrushing machine (MSEt - ELQUIP, São Paulo, Brazil), using machine-fixed brushes (Curaprox, Curaden Switzerland). A total of 20,000 brushing cycles were carried out with a load of 300 g at 180 cycles/min. A dilution of the dentifrice (Colgate Total 12, Colgate-Palmolive Co., São Paulo, Brazil) was used from 1 part to 3 parts deionized water.²² After the abrasion cycles, the loss of structure was evaluated using software (Proscan Application software v.2.0.17) to calculate the depth of the test area in relation to the reference areas.

Statistical analysis

The DC, flexural strength, and profilometry data were submitted to analysis of variance and Tukey's test ($\alpha = 0.05$) after an analysis of homoscedasticity. The FM data were heteroscedastic and were evaluated

through the nonparametric Kruskal–Wallis test. A p-value < 0.05 was considered significant.

Results

Characterization of the particles

The formation of DCPD crystalline structures was confirmed by the diffractograms with peak intensities at 11.6°, 20.9°, 23.6°, 29.3°, 35.5°, and 48°, respectively. The numerical results obtained in the characterization analyses (adsorption isotherms with the BET method and theoretical density) of the particles are presented in Table 1.

The inversion of the receptor solution at the time of synthesis, together with functionalization of the particles, had effects on the surface area of the particles. With the ammonium phosphate solution as a receptor (AP_ab, AP_ap, and AP_nf groups), the moment the monomer was added and the presence of the functionalizing agent did not significantly affect particle surface area. However, when the calcium nitrate solution was the receptor solution (CN_ab, CN_ap and CN_nf groups), the DCPD particles presented a surface area up to 4.8 times higher when they were functionalized. In addition, the functionalization of the particles at the time of synthesis led to the formation of particles with the largest surface area (CN_ab group: 43 m²/g, functionalization after synthesis CN_ap group: 25 m²/g).

The theoretical density results allowed us to estimate the percentage of functionalizing monomer present in the particles, which varied between 38% and 59%. Figure shows the images obtained by scanning electron microscopy. Functionalized particles with similar appearance on thin plates

Table 1. Characterization of DCPD particles according to synthesis conditions.

Groups	Receiving solution	Functionalization	Density (g/mL)	TEGDMA content (%)	Surface area (m ² /g)	Particle long axis (μm)	Particle width (μm)
AP_ab	Ammonium	<i>ab initio</i>	1.8	59	27	19	7
AP_ap	phosphate	after precipitation	2.0	47	26	20	7
AP_nf		-	2.8	-	20	21	9
CN_ab	Calcium	<i>ab initio</i>	2.1	38	43	19	8
CN_ap	nitrate	after precipitation	1.9	50	25	22	10
CN_nf		-	2.7	-	9	29	11

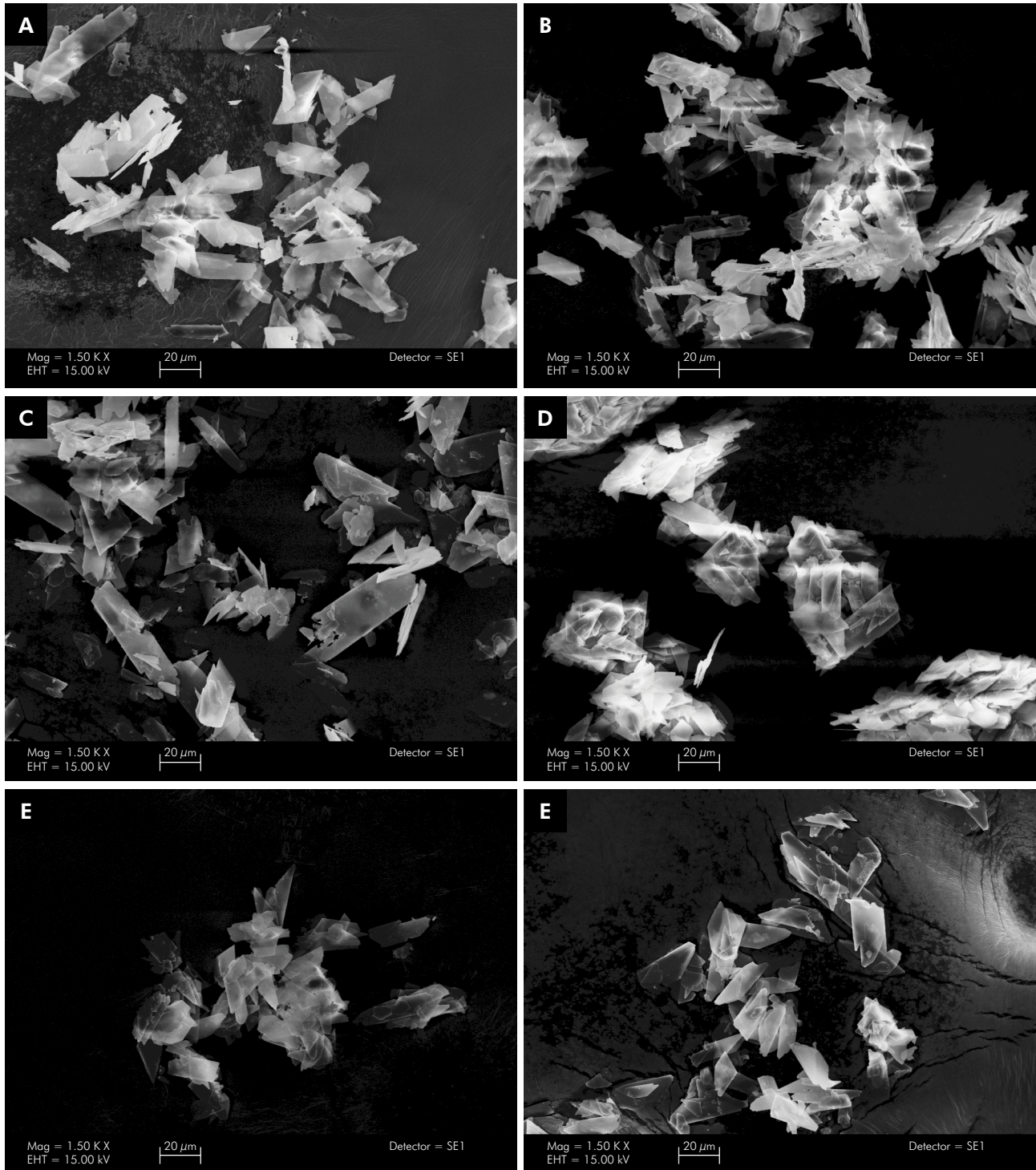


Figure. Scanning electron microscopic images of the groups of synthesized particles, with an increase of 1,500 times. A–C present particles synthesized with the ammonium phosphate solution as the receptor, functionalized during (AP_ab) or after synthesis (AP_ap) or without a functionalizing agent (AP_nf); and D–F illustrate the particles synthesized with the calcium nitrate solution as the receptor, functionalized during (CN_ab) or after synthesis (CN_ap) or without functionalizing (CN_nf).

Table 2. Means, standard deviations and statistical analysis of experimental groups submitted to biaxial flexural test and roughness analysis.

Groups	Degree of conversion (%)	Biaxial flexural strength (MPa)	Flexural modulus (GPa)	Surface roughness (μm)
CN_ab	80.7 (2.4) ^A	122.5 (28.7) ^A	3.6 (2.4) ^B	2.0 (0.8) ^A
CN_ap	83.9 (4.0) ^A	86.9 (15.0) ^B	6.3 (1.6) ^{AB}	1.6 (0.7) ^A
CN_nf	80.9 (1.3) ^A	83.0 (14.6) ^B	8.7 (4.3) ^A	1.8 (0.6) ^A
Barium glass	77.6 (1.8) ^A	142.4 (23.3) ^A	5.8 (1.7) ^{AB}	2.3 (1.2) ^A

contained average dimensions of 20 ± 10 mm in the long axis and 8 ± 3 mm in width. The nonfunctionalized particles were slightly larger with average dimensions of 25 ± 12 mm in length and 10 ± 4 mm in width.

Incorporation of the particles in the resin-based material

The BFS, FM, and surface roughness results are presented in Table 2.

All tested materials had a similar DC ($p > 0.05$). Only the CN_ab group presented strength similar to the control, while the CN_ap and CN_nf groups revealed flexural strength similar to each other but significantly lower than the CN_ab and control groups ($p < 0.001$). The only significant difference in the FM was detected between the CN_nf and CN_ab groups ($p < 0.05$). Surface roughness varied between $1.6 \mu\text{m}$ and $2.3 \mu\text{m}$, and was similar among the groups ($p > 0.05$).

Discussion

A previous study reported an increase in the surface area of DCPD particles when TEGDMA was added to the synthesis *ab initio*.¹⁷ The present results confirm that finding and highlight the effect of a receptor solution on particle surface area. Furthermore, the presence of the monomer did not prevent the formation of DCPD, regardless of the drip solution, according to XRD.

The variables evaluated in this study did not affect the percentage of TEGDMA present on the DCPD particles. However, even with similar percentages of TEGDMA, surface area values were quite distinct, particularly for the CN_ab and CN_ap

groups. Incorporating the functionalizing monomer into the receptor solution (prior to the reaction) may have produced particles with a larger area because TEGDMA has low acidity and can bind by chemisorption to the surface of particles, affecting their growth. However, this effect was only observed when the calcium nitrate solution was the receptor. The comparative analysis of the surface area results of the CN_ab and CN_ap groups suggested that incorporating the functionalizing agent after synthesis led to physical adsorption of the monomer on already formed DCPD particles. Considering the larger surface area of the particles obtained in the CN_ab group, the second phase of this study followed the application of the particles, which were synthesized with calcium nitrate as the receptor solution in a resinous organic matrix.

DCPD has two main characteristics that makes it suitable as ion-releasing particles in resin-based materials: a) DCPD has intermediate solubility among the phases of calcium orthophosphates,²³ which favors ion release and b) the refractive index of the DCPD particles is 1.54/1.55, which is very close to the refractive indices of the resin matrix (1.50–1.55)¹⁵ and ensures light transmission during photopolymerization. The 20% volume fraction of added particles was determined by using the results obtained in an earlier *in vitro* study, as a reference in which materials containing percentages of 10 vol% and 20 vol% of functionalized DCPD particles remineralized enamel lesions.⁴

Incorporating DCPD particles, regardless of functionalization, did not significantly affect the DC due to the compatibility of the refractive indices already discussed. Therefore, the results obtained from other tests cannot be attributed to

differences in the DC. Studies that have evaluated materials containing other bioactive particles, such as unsilanized bioglass, have reported that incorporating similar percentages of particles causes a significant decrease in the DC value.²⁴ In previous studies, resin-based materials, which also contained 20% DCPD particles functionalized *ab initio* with TEGDMA, had lower flexural strength values than those found in this study.¹³ The DCPD particles in the previous study presented a lower TEGDMA percentage (8%), resulting in a higher effective DCPD content in the material, which may explain the difference in the results. The BFS values of the CN_ab and control groups were similar. This result is very promising as it demonstrates that the DCPD particles possibly did not behave as material defects, and provided mechanical characteristics similar to material with a reinforcing filler.

It is well established that the interfacial bonds between the inorganic particles and the organic phase of composites are necessary to increase their mechanical strength because of the more efficient stress transfer mechanism between the particles and the resin matrix.²⁵ However, the CN_ap group particles were functionalized and the strength value (87 MPa) was similar to that of the group of nonfunctionalized particles (CN_nf group, 83 MPa). A possible explanation for this finding may be that incorporating particles with a larger total surface area (group CN_ab) promoted a better interaction with the resin matrix. Notably, the differences observed in surface area among particles do not necessarily correspond to a smaller size on SEM, as these measurements represent a very small sample. Another hypothesis is related to the effective volume of DCPD particles present in the material is that a lower percentage of DCPD means a higher percentage of functionalizing monomer, which could in itself improve the mechanical behavior of the material. A similar mechanism is observed in composites containing bioglass, in which more adverse effects are observed in the flexural strength value when the percentage of bioglass is increased.²⁶

The modulus of elasticity of a material is related to the stiffness of the particles and to the way they

interact with each other in the resinous material.²⁷ All materials containing DCPD particles presented FM values similar to the control group, with values between 3.6 and 8.7 GPa obtained for the CN_ab and CN_nf groups ($p < 0.05$). The observed difference between the particle densities, and consequently in the percentage of functionalized monomer, may be a contributing factor to the difference in modulus values considering that particles with higher density values increase the modulus values.²⁸

This study also presents results of an evaluation of the roughness of resinous matrices containing DCPD after an abrasive challenge. The 20,000 cycles of brushing resembled approximately 2 years of brushing.²⁹ The mechanical wear of the composites was reported as gradual removal of the polymeric matrix,²⁹ in which unsupported fillers become more susceptible to exfoliation.³⁰ No significant differences in the surface roughness values were observed between the groups after the abrasive challenge (1.6–2.3 μm), even with a significant difference between the sizes of the barium glass particles and the DCPD particles. The DCPD particles may have fractured during the abrasion challenge due to their low hardness, regardless of particle size.

Conclusions

Considering the limitations of this study, we conclude that the calcium nitrate solution, as a receptor at the moment of synthesis, allowed the formation of higher surface area DCPD particles. Within these groups of particles (CN_ab, CN_ap, and CN_nf), the timing and presence of particle functionalization did not affect the DC or surface roughness after the abrasive challenge. In the BFS analysis, the resin with DCPD particles functionalized *ab initio* presented a behavior similar to that of resin containing conventional barium glass particles in a 20% volume.

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