

# Effect of filler level and particle size on dental caries-inhibiting Ca–PO<sub>4</sub> composite

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Received: 7 May 2008 / Accepted: 23 March 2009 / Published online: 14 April 2009  
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**Abstract** Secondary caries and restoration fracture are common problems in restorative dentistry. The aim of this study was to develop Ca–PO<sub>4</sub> nanocomposite having improved stress-bearing properties and Ca and PO<sub>4</sub> ion release to inhibit caries, and to determine the effects of filler level. Nanoparticles of dicalcium phosphate anhydrous (DCPA), two larger DCPA powders, and reinforcing whiskers were incorporated into a resin. A 6 × 3 design was tested with six filler mass fractions (0, 30, 50, 65, 70, and 75%) and three DCPA particle sizes (112 nm, 0.88 μm, 12.0 μm). The DCPA nanocomposite at 75% fillers had a flexural strength (mean ± SD; *n* = 6) of 114 ± 23 MPa, matching the 112 ± 22 MPa of a commercial non-releasing, hybrid composite (*P* > 0.1). This was 2-fold of the 60 ± 6 MPa of a commercial releasing control. Decreasing the particle size increased the ion release. Increasing the filler level increased the ion release at a rate faster than being linear. The amount of ion release from the nanocomposite matched or exceeded those of previous composites that released supersaturating levels of Ca and PO<sub>4</sub> and remineralized tooth lesions. This suggests that the much stronger nanocomposite may also be effective in remineralizing tooth

lesion and inhibiting caries. In summary, combining calcium phosphate nanoparticles with reinforcing co-fillers in the composite provided a way to achieving both caries-inhibiting and stress-bearing capabilities. Filler level and particle size can be tailored to achieve optimal composite properties.

## 1 Introduction

Dental resin composites are composed of reinforcing fillers in a resinous matrix that is polymerized to form a solid restoration [1–4]. Recent reports show that secondary caries and restoration fracture remain the two most common problems: “The two main challenges are secondary caries and bulk fracture” [5–7]. Restoration replacement accounts for more than 50% of all operative work [8], and replacement dentistry costs about \$5 billion/year in the US [9]. While resin compositions, fillers types, and cure conditions have been significantly studied [10–13], there is still room for improvement to achieve higher fracture resistance and inhibit secondary caries, in order to increase the longevity of composite restorations.

Calcium phosphate (CaP) based biomaterials are important for hard tissue repair due to their excellent biocompatibility and bioactivity [14–17]. Dental composites filled with CaP particles have been developed to combat caries [18–21]. Several CaP phases are regarded as biological precursors that form initially and then transform to apatites [22]. Hydroxyapatite [HA: Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>], the structural prototype of the major mineral component of teeth and bones, is the final stable product in the precipitation of calcium and phosphate ions in neutral or basic solutions (pH of 7–9 at 37°C) [22]. Hence there is a wide range of solution conditions when the precipitation of HA

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occurs spontaneously. Indeed, several composites released supersaturating levels of calcium (Ca) and phosphate ( $\text{PO}_4$ ) ions in aqueous solutions, which then precipitated to form HA [18–21]. These composites were shown to effectively remineralize enamel and dentin lesions in vitro [18, 21].

However, these CaP composites are relatively weak mechanically and do not possess sufficient load-bearing capabilities. For example, a CaP composite had a flexural strength of about half of the strength of the unfilled resin [19]. Such a low strength was “inadequate to make these composites acceptable as bulk restoratives” [20].

Composites containing nano-silica-fused whiskers were recently developed with strength and fracture toughness nearly 2-fold those of commercial composites [23]. The whisker composites showed superior performance in thermal cycling [24], water-aging [25], and three-body wear [26]. The whisker composite was non-cytotoxic and supported cell proliferation in vitro [27]. Nanoparticles of dicalcium phosphate anhydrous ( $\text{CaHPO}_4$ , or DCPA) were synthesized and incorporated into dental composites for the first time [28–30]. These nanocomposites possessed high mechanical properties while maintaining Ca and  $\text{PO}_4$  release to combat tooth decay [30, 31]. A recent study examined the effects of DCPA particle size and silanization on composite properties [32]. In that study, a single filler level of 65% was tested [32]. In addition, other previous studies on CaP composites have not investigated the filler level effect. For example, a study on CaP filled dental composite used a single filler level of 73% by mass [21]. Another study on amorphous calcium phosphate composite used a single filler level of 40% by mass [20]. A systematic study on the effects of CaP filler level, coupled with various CaP particle sizes, on dental composite properties remains to be performed.

Accordingly, the present study investigated the effect of filler level on the Ca and  $\text{PO}_4$  ion release and mechanical properties of dental composite, using three different DCPA particle sizes (112 nm, 0.88  $\mu\text{m}$ , and 12  $\mu\text{m}$ ), and six different filler levels (from 0 to 75%). The aim of this study was: (1) to develop a series of CaP composites with various filler levels having improved mechanical properties and sustained ion release; and (2) to determine the effects of filler level and particle size on composite mechanical and ion release properties.

## 2 Materials and methods

### 2.1 Fillers

Previous studies on CaP composites used single particle sizes (e.g., a particle size of 1.1  $\mu\text{m}$  for DCPA) [21], without varying the particle size. Furthermore, while nanoparticles

of HA and tricalcium phosphate were synthesized previously [33, 34], nanoparticles of DCPA were synthesized only recently in our laboratory for the first time [28–30]. This enabled the comparison of DCPA nanoparticles with its traditional counterparts in a dental resin. The DCPA nanoparticles were synthesized via a spray-drying technique [28–30]. X-ray diffraction indicated that the collected powder was DCPA [30]. The specific surface area of the DCPA nanopowder was measured using multipoint-BET (AUTOSORB-1, Quantachrome, Boynton Beach, FL) to be 18.6  $\text{m}^2/\text{g}$ , yielding a mean particle size of 112 nm [30].

A commercial DCPA powder (J. T. Baker Chemical, Phillipsburg, NJ) was also used. The particle size distribution was measured by a sedimentation method with the use of a centrifugal particle analyzer (SA-CP3, Shimadzu, Kyoto, Japan). The as-received DCPA powder had a particle size ranging from 1 to 60  $\mu\text{m}$ , with a median (50% by mass) particle size of 12.0  $\mu\text{m}$ . To obtain a finer powder, the as-received DCPA was ball-milled (Retsch PM4, Brinkman, NY) in ethanol for 24 h to obtain a fine DCPA powder. This ground DCPA had a particle size range of 0.1–5  $\mu\text{m}$ , with a median of 0.88  $\mu\text{m}$ . These particles were incorporated into a dental resin at a single filler level mass fraction of 65% in a previous study [32]. The present study will vary the filler level from 0 to 75%.

These three DCPA powders, namely, nano DCPA (112 nm), ground commercial DCPA (0.88  $\mu\text{m}$ ), and as-received commercial DCPA (12.0  $\mu\text{m}$ ), were used to fabricate composites.

As a co-filler, silicon nitride whiskers ( $\alpha\text{-Si}_3\text{N}_4$ , Nanostructured and Amorphous Materials, Los Alamos, NM) were used to improve the mechanical properties of the composite. Because the particle size analyzer yielded only an equivalent spherical diameter, the whiskers were examined using a scanning electron microscope (SEM, 5300, JEOL, Peabody, MA). The average whisker length of 100 randomly-selected whiskers was measured to be 14  $\mu\text{m}$ , with a range of approximately 3–55  $\mu\text{m}$ . The average whisker diameter was 0.5  $\mu\text{m}$ , with a range of 0.1–2.0  $\mu\text{m}$ . The whiskers were mixed with silica (Aerosil-OX50, Degussa, Ridgefield, NJ) having a diameter of about 40 nm, at a silicon nitride:silica mass ratio of 5:1 [23–26]. The mixture was heated at 800°C for 30 min to fuse the nanosilica onto the whiskers [23–26]. The nanosilica roughened the whisker surfaces and enhanced silanization efficacy with improved whisker retention in the resin matrix. The powder was silanized with 4% by mass 3-methacryloxypropyltrimethoxysilane and 2% n-propylamine [26].

### 2.2 Resin composite fabrication

A monomer consisting of mass fractions of 48.975%, by mass, Bis-GMA (bisphenol glycidyl dimethacrylate),

48.975% TEGDMA (triethylene glycol dimethacrylate), 0.050% 2,6-di-*tert*-butyl-4-methylphenol, and 2.000% benzoyl peroxide formed part I, the initiator, of a two-part chemically activated resin [30]. Part II, the accelerator resin, consisted of 49.5% Bis-GMA, 49.5% TEGDMA, and 1.0% *N,N*-dihydroxyethyl-*p*-toluidine.

The fillers consisted of nanosilica-fused whiskers and DCPA at a mass ratio of DCPA:whisker of 1:1, following a previous study [30]. The following filler mass fractions ( $[\text{DCPA} + \text{whiskers}]/[\text{DCPA} + \text{whiskers} + \text{resin}]$ ) were tested: 0% (unfilled resin), 30, 50, 65, 70, and 75%. They were selected because a 30% filler level would be suitable for adhesive applications, a 50–65% filler level could yield crown cement and a flowable composite, and a composite at 70–75% fillers could be used in stress-bearing restorations.

A  $6 \times 3$  full factorial design was tested, with six filler levels, and three different DCPA sizes. Equal masses of the two pastes, part I and part II, were mixed and filled into a rectangular mold with  $(2 \times 2 \times 25)$  mm<sup>3</sup> dimensions. The specimens were incubated at 37°C with a relative humidity of approximately 50% for 24 h prior to testing.

A hybrid composite (TPH, Caulk/Dentsply, Milford, DE) was used as a non-releasing control. It consisted of barium glass and fumed silica with a mean size of about 0.8  $\mu\text{m}$ , at 78% filler level by mass in a urethane-modified Bis-GMA-TEGDMA resin. The specimens were photocured (Triad-2000, Dentsply, York, PA) for 1 min on each open side of the specimen. A releasing control (Vitremmer resin-modified glass ionomer, 3 M, St. Paul, MN) was mixed according to the manufacturer's instructions, filled into the mold, and light cured for 1 min on each open side of the specimen. It was used as another control for mechanical properties.

### 2.3 Flexural testing

Flexural strength and elastic modulus were measured using a three-point flexural test with a 20-mm span at a cross-head-speed of 1 mm/min on a computer-controlled Universal Testing Machine (5500R, MTS, Cary, NC). Flexural strength was calculated:  $S = 3P_{\text{max}}L/(2bh^2)$ , where  $P_{\text{max}}$  is the maximum load on the load-displacement curve,  $L$  is span,  $b$  is specimen width, and  $h$  is specimen thickness [35]. Elastic modulus was calculated by:  $E = (P/d)(L^3/[4bh^3])$ , where load  $P$  divided by the corresponding displacement  $d$  is the slope of the load-displacement curve in the linear elastic region [36].

### 2.4 Ca and PO<sub>4</sub> ion release

To measure Ca and PO<sub>4</sub> ion release from the composite, a NaCl solution (133 mmol/l) buffered with 50 mmol/l

HEPES (pH = 7.4; 37°C) was used to immerse the specimens. Following a previous study [30], three specimens of approximately 2 mm  $\times$  2 mm  $\times$  12 mm were immersed in 50 ml solution, yielding a specimen volume/solution of 2.9 mm<sup>3</sup>/ml. This compared to a specimen volume per solution of approximately 3.0 mm<sup>3</sup>/ml in a previous study [19]. The concentrations of Ca and PO<sub>4</sub> released from the specimens were measured vs immersion time: 1 day (d), 3 d, 7 d, 14 d, 21 d, 28 d, 35 d, 42 d, 49 d, and 56 d. At each time period, aliquots of 0.5 ml were removed and replaced by fresh solution. The aliquots were analyzed for Ca and PO<sub>4</sub> concentrations via spectrophotometric methods (DMS-80 UV-visible, Varian, Palo Alto, CA) following previous studies [19, 21].

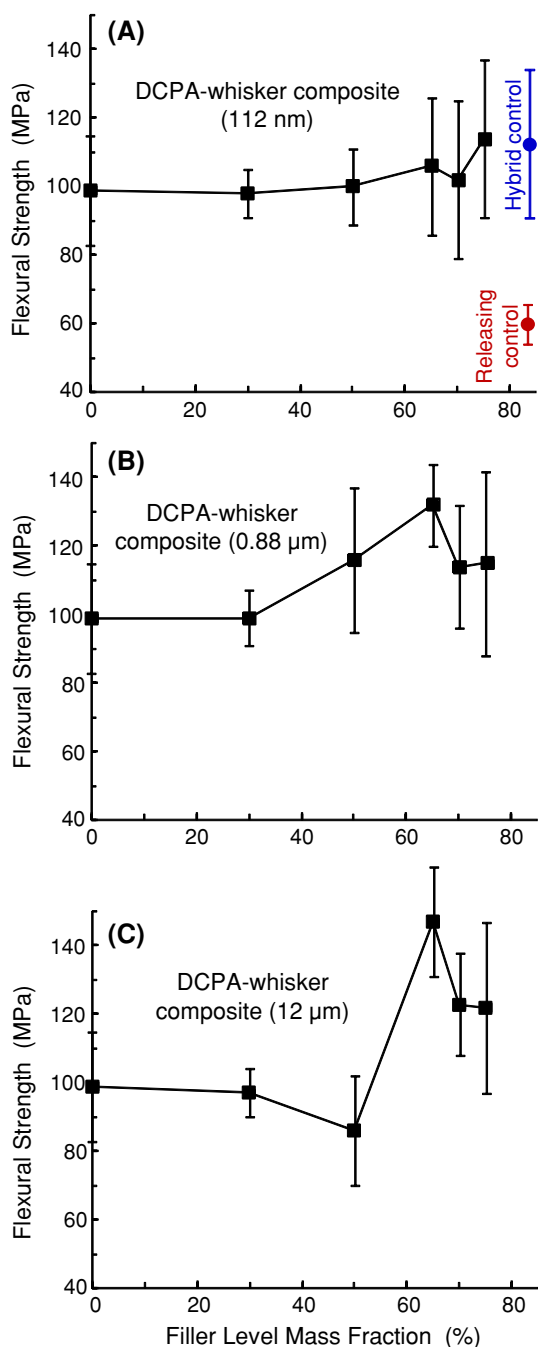
One-way and two-way ANOVA were performed to detect the significant effects of the variables. Tukey's multiple comparison test was used to compare the data at a  $P$  value of 0.05.

## 3 Results

Figure 1 plots the flexural strength (mean  $\pm$  SD;  $n = 6$ ) for the  $6 \times 3$  design. Two-way ANOVA showed significant effects of particle size and filler level ( $P < 0.05$ ), with a significant interaction between the two parameters ( $P < 0.05$ ). For the nanocomposite, increasing the filler level had no significant effect on strength ( $P > 0.1$ ). For the composite with 0.88- $\mu\text{m}$  DCPA, the strength at 65% was significantly higher than those at 0 and 30% ( $P < 0.05$ ). For the composite with 12- $\mu\text{m}$  DCPA, the strength at 65% was higher than those at 0, 30 and 50% ( $P < 0.05$ ). DCPA-whisker composites matched the  $112 \pm 22$  MPa of the non-releasing hybrid control ( $P > 0.1$ ). They had strengths higher than the  $60 \pm 6$  MPa of the releasing control ( $P < 0.05$ ).

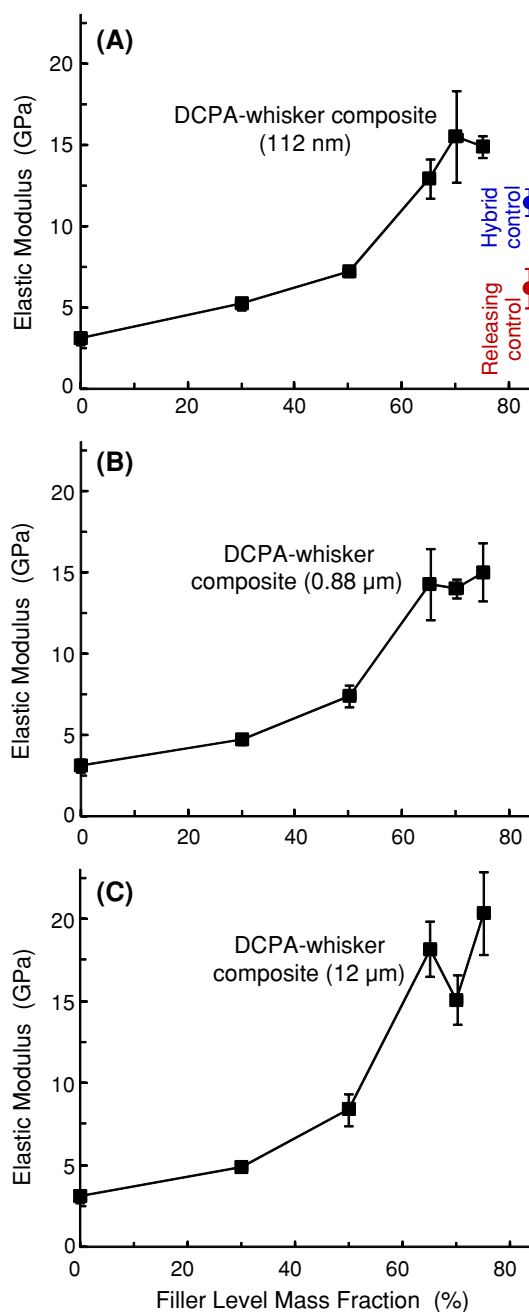
In Fig. 2, increasing the filler level increased the elastic modulus for all three DCPA sizes ( $P < 0.05$ ). The composites with different DCPA sizes at the same filler level generally had similar moduli, except for the 12- $\mu\text{m}$  DCPA composite that had slightly higher moduli. The elastic moduli (mean  $\pm$  SD;  $n = 6$ ) for the DCPA-whisker composites at 75% filler level ranged from  $14.9 \pm 0.7$  to  $20.4 \pm 2.5$  GPa, significantly higher than  $11.7 \pm 0.4$  GPa of the commercial non-releasing control, and  $5.2 \pm 0.7$  of the releasing control ( $P < 0.05$ ).

Figure 3 shows the cumulative phosphate ion release from the composites. In each plot, the label at the right side indicates the composite filler level. As expected, the unfilled resin (0%) and the hybrid control had no detectable ion release. Increasing the immersion time from 1 to 56 days increased the ion concentration



**Fig. 1** Flexural strengths for the  $3 \times 6$  full factorial design (with three different DCPA particle size and six filler levels in the resin composite). Each value is the mean of six measurements with the error bar showing one standard deviation (mean  $\pm$  SD;  $n = 6$ )

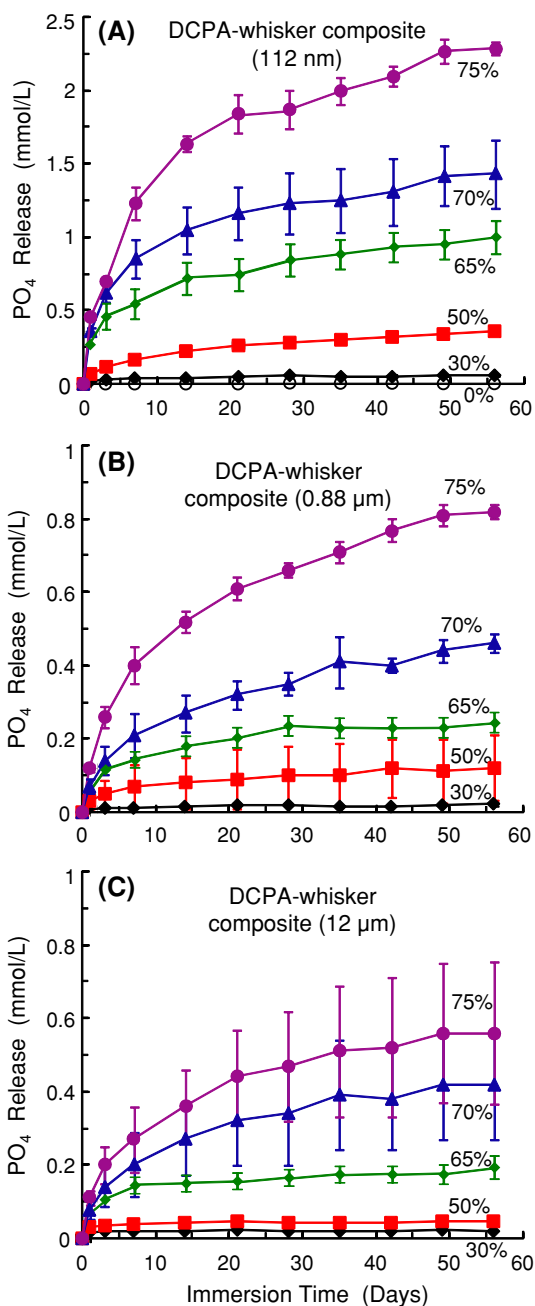
( $P < 0.05$ ). For each DCPA size (each plot), increasing the filler level increased the amount of release ( $P < 0.05$ ). For example, the composite with 112-nm DCPA had a phosphate concentration at 56-day of  $2.28 \pm 0.07$  mmol/l at 75% filler level,  $1.43 \pm 0.23$  at 70% fillers,  $0.36 \pm 0.01$  at 50% fillers, and  $0.06 \pm 0.01$  at 30% fillers. These



**Fig. 2** Elastic modulus of the composites. Increasing the filler level significantly increased the modulus for all three DCPA sizes ( $P < 0.05$ ). Each value is mean  $\pm$  SD;  $n = 6$

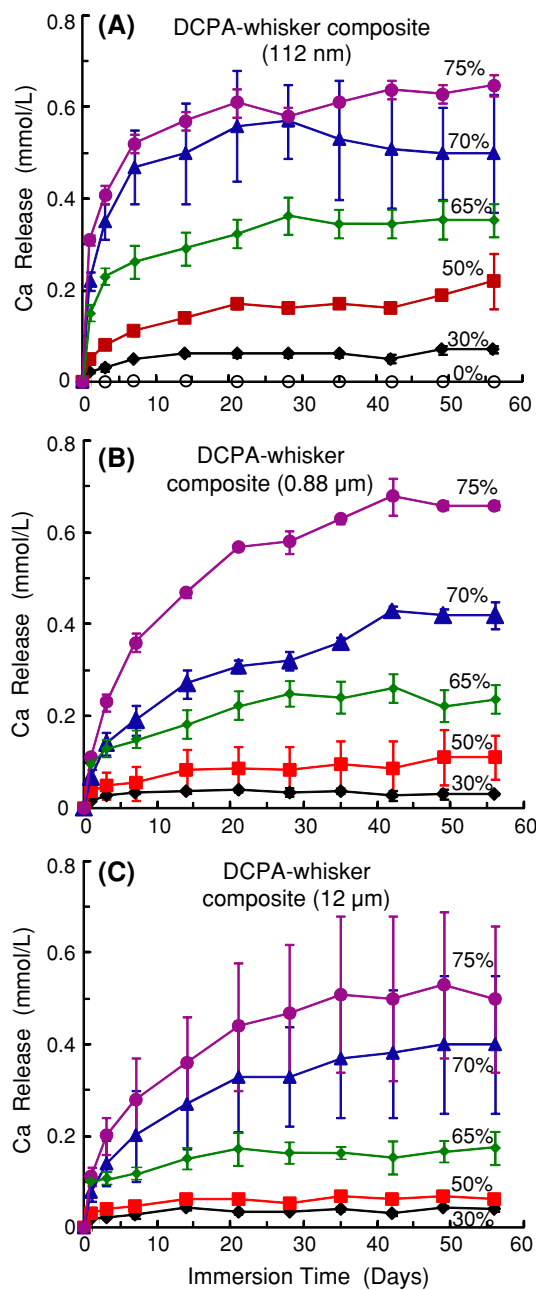
values are significantly different from each other (Tukey's at 0.05).

Different DCPA sizes had a significant effect on the release ( $P < 0.05$ ). The 56-day  $\text{PO}_4$  release was  $2.28 \pm 0.07$  mmol/l for the composite with 112-nm DCPA, significantly higher than  $0.82 \pm 0.02$  for the composite with 0.88- $\mu\text{m}$  DCPA, and  $0.56 \pm 0.19$  with 12- $\mu\text{m}$  DCPA, all at the same filler level of 75% ( $P < 0.05$ ).



**Fig. 3** PO<sub>4</sub> ion release from the composite with **a** the nano-DCPA (112 nm); **b** the ground commercial DCPA (0.88 μm); and **c** the as-received commercial DCPA (12 μm). Each values is mean ± SD; *n* = 3. The label at the right side indicates the filler level. The DCPA:whisker mass ratio was 1:1. Note the y-axis scale difference between the plots

Figure 4 plots the corresponding Ca ion release. Increasing the filler level and immersion time significantly increased the release (*P* < 0.05). However, the cumulative Ca release appeared to plateau over time when it reached about 0.65 mmol/l. The 56-day Ca release for the composite



**Fig. 4** Ca ion release from composite with **a** the nano-DCPA (112 nm); **b** the ground commercial DCPA (0.88 μm); and **c** the as-received commercial DCPA (12 μm). Each values is mean ± SD; *n* = 3. In each plot, the label at the right side indicates the filler level. The DCPA:whisker mass ratio was 1:1. Increasing the filler level and immersion time significantly increased the amount of Ca release (*P* < 0.05)

with 112-nm DCPA at 75% filler level was 0.65 ± 0.02 mmol/l, not significantly different from 0.63 ± 0.01 mmol/l with 0.88-μm DCPA, and 0.49 ± 0.16 mmol/l with 12-μm DCPA (*P* > 0.1).

## 4 Discussion

### 4.1 Combination of caries-inhibiting and stress-bearing capabilities

Previous studies developed novel CaP composites for Ca and PO<sub>4</sub> ion release to combat tooth decay [20, 21], but the effects of CaP filler level on composite properties were not investigated. Currently available restoratives in general address only either the caries-inhibiting issue, or the load-bearing issue, but not both issues. For example, commercial composites similar to the hybrid control of the present study are used in stress-bearing restorations, but with no ion release to combat caries. On the other hand, commercial releasing restoratives are mechanically too weak for large stress-bearing posterior restorations. Previous studies on CaP composites [18–21] showed that when the Ca and PO<sub>4</sub> ions were released from the composite restoration, they reprecipitated to form hydroxyapatite outside the composite and inside the tooth lesions, significantly increasing the mineral content of the lesion, thereby remineralizing the lesion. Hence, these CaP composites are promising for caries inhibition. Using specimens without water immersion, previous studies reported that an ACP (amorphous calcium phosphate) composite had a flexural strength of 56 MPa [19, 37]. This was consistent with the observation that “all the amorphous calcium phosphate fillers yielded polymerized materials weaker than unfilled polymers” [19]. Another composite containing traditional DCPA particles of about 1 μm in size had a flexural strength of around 40–50 MPa for specimens without water immersion [21, 38]. Note that these values are similar to that of the commercial releasing control in Fig. 1. Also note that in Fig. 1, the strength generally did not significantly depend on the DCPA particle size. This is likely because the DCPA particles did not reinforce the resin; in fact, previous studies showed that these CaP fillers decreased the composite strength to be about half of the strength of the unfilled resin [19, 21]. The composites in Fig. 1 had strengths matching or higher than the strength of the unfilled resin, because the whiskers provided the reinforcement. Since it was the whiskers, not the DCPA, that provided the strength, the DCPA particle size had no significant effect on composite strength. Another point worth noting is that although the composite strength was rather similar to that of the unfilled resin (Fig. 1), the elastic modulus of the composite was much higher than that of the unfilled resin (Fig. 2). The modulus was important in composite wear and load-bearing properties [26].

In the present study, combining CaP nanoparticles with reinforcing fillers in the resin achieved caries-inhibiting and stress-bearing capabilities. The nanocomposite containing 75% fillers (with 37.5% nano-DCPA and 37.5% whiskers)

had a flexural strength (114 MPa) matching that of a commercial non-releasing hybrid composite (112 MPa). However, immersion in water can degrade the mechanical properties of the composite, especially for composites with Ca and PO<sub>4</sub> release and filler dissolution. For example, the ACP composite's flexural strength decreased to 40 MPa after only 11 days of immersion [18, 19, 37]. The flexural strength of another traditional CaP composite decreased to 10–20 MPa after 90 days of immersion [38]. A major difference between the traditional CaP composites and the new composites of the present study was that, the traditional CaP composites contained only CaP fillers, while the composites of the present study contained not only CaP fillers, but also reinforcing whiskers that were stable and did not degrade during water immersion. While the present study focused on the effects of particle size and filler level without examining the effect of immersion, our previous study did measure the strength of whisker-reinforced nanocomposites with Ca and PO<sub>4</sub> release before and after immersion [30]. That study showed that in general, there was a strength loss of approximately 20% after water immersion for 2 months, with flexural strengths of 80–100 MPa after immersion for the whisker-reinforced CaP nanocomposites [30]. These strengths were 2–3 fold higher than the traditional CaP composites. This was likely because the nanosilica-fused whiskers were strong and did not degrade, and were bonded with the resin matrix [24–27]. Hence the whisker-CaP nanocomposites are expected to have higher water-aging durability than traditional CaP composites that contained only releasing fillers without stable reinforcing fillers. Further studies are needed to investigate the long-term (e.g., longer than a year) water-aging behavior of the CaP composites of the present study.

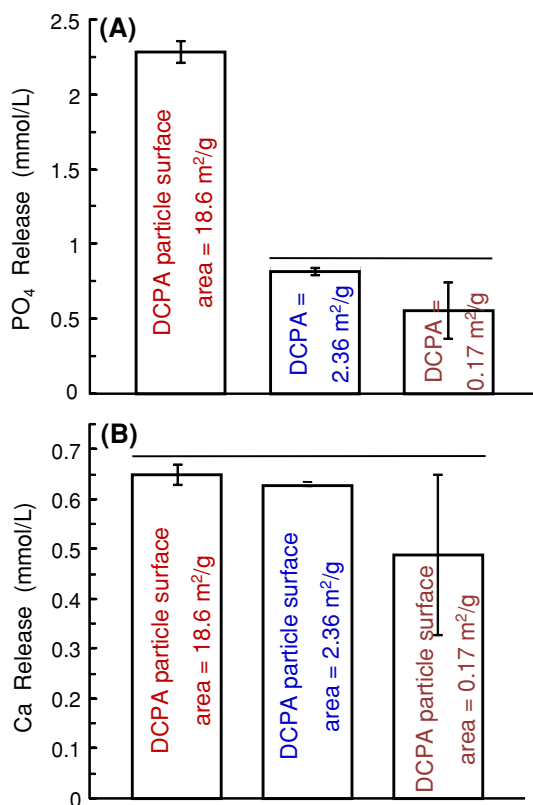
While the strength of the nanocomposite was 2-fold that of previous CaP composites, the amounts of release exceeded or matched the previous values. ACP composites yielded a Ca concentration of 0.3–1.0 mmol/l, and a PO<sub>4</sub> concentration of 0.2–0.7 mmol/l (Figs. 2, 3 in Ref. [19]). Another CaP composites had a Ca concentration of 0.5 mmol/l, and PO<sub>4</sub> of 0.1 mmol/l in buffered saline [21]. Measured using a similar method, the mechanically-strong nanocomposite of the present study had a comparable Ca concentration of 0.65 mmol/l, and a PO<sub>4</sub> concentration of 2.28 mmol/l. The fact that the Ca and PO<sub>4</sub> concentrations from the nanocomposite matched or exceeded those of the previous CaP composites suggests that the nanocomposite may also be effective in remineralizing tooth lesion and inhibiting caries.

### 4.2 Effect of CaP particle size

A reason for the high ion release is the smaller nanoparticles, yielding a higher surface area at the same filler level.

The CaP nanoparticles had much higher surface area than the traditional CaP particles. For example, in a previous study [21], the DCPA particle size was 1.1  $\mu\text{m}$ , and the TTCP (tetracalcium phosphate) particle size was 16  $\mu\text{m}$ . The specific surface area  $A = 6/(d\rho)$ , where  $d$  is the equivalent spherical diameter, and  $\rho$  is density (2.89  $\text{g}/\text{cm}^3$  for DCPA, and 3.07  $\text{g}/\text{cm}^3$  for TTCP). Hence the specific surface area was estimated to be approximately 1.9  $\text{m}^2/\text{g}$  for DCPA, and 0.12  $\text{m}^2/\text{g}$  for TTCP. In contrast, the nano-DCPA had an  $A = 18.6 \text{ m}^2/\text{g}$ , 1–2 orders of magnitude higher than the previous values. The higher surface area of the nanoparticles appeared to facilitate the ion release. Figure 5a plots the  $\text{PO}_4$  release at 56-day with 75% filler level for the three composites having DCPA surface area of 18.6  $\text{m}^2/\text{g}$  (112 nm), 2.36  $\text{m}^2/\text{g}$  (0.88  $\mu\text{m}$ ), and 0.17  $\text{m}^2/\text{g}$  (12  $\mu\text{m}$ ), demonstrating the effect of particle surface area.

On the other hand, the Ca release was only slightly increased when the particle surface area was increased (Fig. 5b). The Ca release plateaued when the concentration reached about 0.65  $\text{mmol}/\text{l}$ . It should be noted that this value is comparable to previous composites shown to effectively remineralize tooth lesions [18–21]. DCPA



**Fig. 5** Effect of calcium phosphate particle size on ion release. **a**  $\text{PO}_4$  release at 56-day with 75% filler level for the three composites having DCPA particle surface area of 18.6  $\text{m}^2/\text{g}$  (particle size = 112 nm), 2.36  $\text{m}^2/\text{g}$  (0.88  $\mu\text{m}$ ), and 0.17  $\text{m}^2/\text{g}$  (12  $\mu\text{m}$ ), demonstrating the significant effect of particle surface area. **b** Corresponding Ca ion release

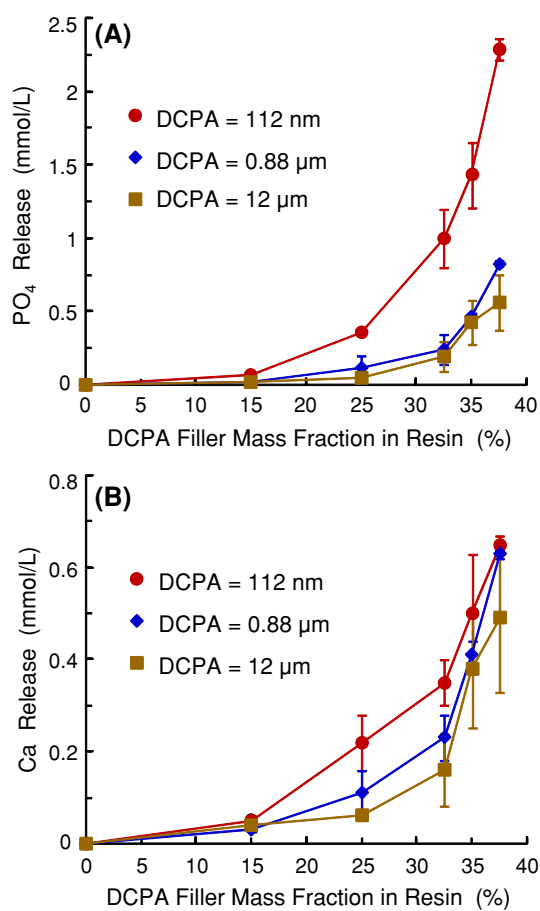
( $\text{CaHPO}_4$ ) has a  $\text{Ca}/\text{PO}_4$  molar ratio of 1:1, hence the released Ca and  $\text{PO}_4$  ratio is expected to approximate 1:1. One possible reason for the Ca concentration of the nanocomposite to be lower than its  $\text{PO}_4$  concentration may be that some of the ions had precipitated to form HA [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ]. The formation of HA consumes six  $\text{PO}_4$  but ten Ca ions, hence it would reduce the Ca concentration more than the  $\text{PO}_4$  concentration. The HA precipitation was probably minimal for the 0.88- $\mu\text{m}$  composite and 12- $\mu\text{m}$  composite, due to their lower ion release and lower ion concentrations in the solution (their  $\text{PO}_4$  concentration was only 1/3 that of the nanocomposite). However, the HA precipitation for the nanocomposite was likely significant due to its higher release and ion concentrations, thus leading to its deviation in the Ca/P ratio. Further studies are needed to verify the HA precipitation.

#### 4.3 Effect of CaP filler level

With the DCPA:whisker ratio = 1:1, the DCPA filler levels in the composite were: 0, 15, 25, 32.5, 35, and 37.5%. Increasing the DCPA filler level significantly increased the Ca and  $\text{PO}_4$  release. This is shown in Fig. 6, where the ion release after 56 days was plotted vs DCPA filler level for the three composites with DCPA sizes of 112 nm, 0.88  $\mu\text{m}$ , and 12  $\mu\text{m}$ , respectively. The data indicate that the ion release increased with increasing filler level at a rate faster than being linear. For example, when the DCPA filler level was increased from 25 to 37.5% (less than 2-fold), the  $\text{PO}_4$  release was increased by 5–7 fold, and the Ca release was increased by 3–6 fold. The ion release increased at a rate faster than being linearly proportional to the filler level, likely because of the following reasons. First, with increasing filler level, the amount of releasing particles in the resin was increased. Second, the interfaces between the fillers and the resin matrix also increased, which likely served as easier passageways for the diffusing-in of water and the diffusing-out of ions. Third, increasing the filler level slightly decreased the polymerization conversion [39]. Therefore, the higher filler level not only increased the sources for release, but also enhanced the diffusion of water and ions through the resin via the increased interfacial areas and the somewhat decreased polymerization conversion. These factors likely contributed to the increase in ion release at a rate faster than being linearly proportional to the filler level.

#### 4.4 Potential clinical applications

DCPA-whisker nanocomposite with about 30% fillers may be suitable for use as Ca and  $\text{PO}_4$  releasing tooth cavity liners, adhesives, and pit-and-fissure sealants. Nanocomposite with about 50% fillers may be used as crown cement



**Fig. 6** Effect of calcium phosphate filler level in the composite on release. Ion release after 56 days is plotted versus DCPA filler level for the three composites with DCPA sizes of 112 nm, 0.88 μm, and 12 μm, respectively. The data indicate that the ion release was increased with filler level at a rate faster than being linear

and orthodontic bracket cement, where the remineralization potential is a highly desirable property. Nanocomposite at a filler level of around 65% may be useful as a flowable composite to repair defective margins to remineralize caries margins and avoiding the need to replace the entire restoration. Nanocomposite with about 75% fillers may be useful in load-bearing and caries-inhibiting restorations. In addition, the Ca and PO<sub>4</sub> releasing composite may be used in combination with fluoride releasing dentifrices and mouthrinses. This may enhance the caries-inhibition and remineralization efficacy via the formation of fluoroapatite with increased resistance to acid attacks. Further research is needed to investigate these applications.

#### 4.5 Summary

The present study examined the filler level effect on CaP composites using different DCPA particle sizes. Composites that possessed a combination of caries-inhibiting and stress-bearing capabilities were formulated. The CaP

nanocomposite had a flexural strength matching that of a commercial non-releasing, hybrid composite. This strength was 2-fold that of a commercial releasing control and previous CaP composites. Decreasing the particle size increased the ion release. Increasing the CaP filler level increased the release at a rate faster than being linear. The Ca and PO<sub>4</sub> release from the nanocomposite matched or exceeded those of previous CaP composites known to remineralize tooth lesions. Potential applications include Ca and PO<sub>4</sub> releasing cavity liners, adhesives, pit-and-fissure sealants, crown cement, flowable composite to repair defective margins, as well as stress-bearing and caries-inhibiting restorations.

**Acknowledgments** We thank Dr. J. M. Antonucci for discussions, A. A. Giuseppetti for assistance, and Esstech (Essington, PA) for providing the resins. This study was supported by NIH R01 DE14190 (Xu), DE17974 (Xu) and DE16416 (Chow), Maryland Nano-Biotechnology Award (Xu), University of Maryland Dental School, NIST, and the ADAF.

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