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## Nano DCPA-Whisker Composites with High Strength and Ca and PO<sub>4</sub> Release

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### Abstract

The main challenges facing composite restorations are secondary caries and bulk fracture. The objective of this study was to develop nano DCPA (dicalcium phosphate anhydrous)-whisker composites with high strength and Ca and PO<sub>4</sub> ion release to combat caries. Flexural strength for the nano DCPA-whisker composites at a nano DCPA:whisker mass ratio of 1:2 ranged from (148 ± 9) MPa to (167 ± 23) MPa, significantly higher than the (103 ± 32) MPa of an inlay/onlay commercial control composite without Ca-PO<sub>4</sub> release. The nano DCPA-whisker composite released PO<sub>4</sub> to a concentration of (1.95 ± 0.13) mmol/L and Ca of (0.68 ± 0.05) mmol/L. Compared with previous conventional Ca- and PO<sub>4</sub>-releasing composites, the nano DCPA-whisker composites had strengths two-fold higher, and released comparable or higher levels of Ca and PO<sub>4</sub>. In conclusion, combining nano-DCPA with whiskers yielded novel composites that released high levels of Ca and PO<sub>4</sub> requisite for remineralization. These high-strength composites may provide a unique combination of stress-bearing and caries-inhibiting capabilities.

### Keywords

dental resin composite; nano particles; whiskers; strength; Ca and PO<sub>4</sub> ion release

## INTRODUCTION

Extensive efforts have been made to improve the fillers and filler-matrix interfaces of resin composites (Söderholm *et al.*, 1984; Goldberg *et al.*, 1994; Ferracane *et al.*, 1998; Drummond and Bapna, 2003; Anusavice *et al.*, 2005). Resin compositions and cure conditions have also been improved (Eick *et al.*, 1993; Bayne *et al.*, 1998; Loza-Herrero *et al.*, 1998). Nonetheless, while composites may be satisfactory for smaller restorations, they are not recommended for large stress-bearing restorations (Sakaguchi, 2005). A recent study reported that “clinical data indicate that the two main challenges are secondary caries and bulk fracture” (Sarrett, 2005).

To overcome the fracture problem, investigators have used whiskers to improve composite strength and fracture resistance (Xu *et al.*, 1999). Nano-sized silica particles were fused onto the whiskers to enhance silanization and retention in the resin by roughening the whisker

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surfaces. Compared with glass-particle-filled composites, the whisker composites exhibited superior performance in thermal-cycling (Xu *et al.*, 2002), long-term water-aging (Xu, 2003), and three-body wear (Xu *et al.*, 2004a). The whisker composites were non-cytotoxic and supported cell proliferation and viability *in vitro* (Xu *et al.*, 2004b).

To combat secondary caries, researchers have developed composites with calcium (Ca) and phosphate (PO<sub>4</sub>) ion release (Dickens-Venz *et al.*, 1994; Skrtic *et al.*, 1996a,b; Dickens *et al.*, 2003). These composites demonstrated the ability to remineralize tooth lesions *in vitro*. However, the low strength of these Ca- and PO<sub>4</sub>-releasing composites was “inadequate to make these composites acceptable as bulk restoratives” (Skrtic *et al.*, 2000).

In the present study, nano-sized dicalcium phosphate anhydrous (DCPA, CaHPO<sub>4</sub>) particles were used as fillers with whiskers in resins. DCPA has been extensively used in calcium phosphate cements (Chow, 2000) and Ca- and PO<sub>4</sub>-releasing materials (Dickens *et al.*, 2003). However, while nano forms of hydroxyapatite and tricalcium phosphate have been synthesized previously (Zhang and Gonsalves, 1997; Sutorik *et al.*, 2003; Bow *et al.*, 2004), nano-sized DCPA particles have never been reported. The nano DCPA particles in the present study were synthesized for the first time. It was hypothesized that adding nano-DCPA would result in Ca and PO<sub>4</sub> release for the composite, and adding whiskers would result in strength matching that of control composites without release.

## MATERIALS & METHODS

### Nano DCPA Particles

Nano-sized DCPA was prepared *via* a spray-drying process (Chow *et al.*, 2004). We prepared a solution by dissolving 1.088 g of DCPA (J.T. Baker, Phillipsburg, NJ, USA) in 1 L of an acetic acid at 16 mmol/L concentration to obtain a Ca and PO<sub>4</sub> ionic concentration of 8 mmol/L. The solution was sprayed through a nozzle (PNR America, Poughkeepsie, NY, USA) that was situated on the top of a heated glass column (Fig. 1A). An electrostatic precipitator (MistBuster, AirQuality Engineering, Minneapolis, MN, USA) was connected to the lower end of the column and drew air from the column to create a steady flow of air/mist. The water/volatile acid were evaporated into the dry, heated column and expelled from the precipitator into an exhaust hood. The dried particles were collected by the electrostatic precipitator.

The powder was examined with x-ray diffractometry (XRD, DMAX2200, Rigaku Denki, Woodlands, TX, USA). The specific surface area of the powder was analyzed by multipoint-BET (AUTOSORB-1, Quantachrome Instruments, Boynton Beach, FL, USA) and transmission electron microscopy (TEM, 3010-HREM, JEOL, Peabody, MA, USA). To minimize agglomeration, we ultrasonicated an acetone suspension of the particles, and drops of the suspension were deposited onto the TEM grids.

### Nano-silica-fused Whiskers

Silicon carbide whiskers (ART, Buffalo, NY, USA) having a mean diameter of about 0.9 μm and a mean length of 14 μm were mixed with nano-silica (Aerosil-OX50, Degussa, Ridgefield, NJ, USA), with a particle size of 40 nm, at a whisker:silica mass ratio of 5:1. The mixture was heated at 800°C for 30 min. The powder was silanized with 4% 3-methacryloxypropyltrimethoxysilane and 2% n-propylamine in cyclohexane (all mass fractions). The nano-silica-fused whiskers are hereinafter referred to as whiskers.

## Fabrication of Nano DCPA-whisker Composites

Three groups of specimens were fabricated (Table). A  $3 \times 3$  design was used, with 3 resins (direct-filling with HEMA; direct-filling without HEMA; indirect heat-cured without HEMA) and 3 DCPA:whisker mass ratios (1:2, 1:1, 2:1) (designated as “D:W”).

For group 1, the nano-DCPA and whiskers were blended with resin part 1 to form the initiator paste (Table). The filler mass fraction was 60% for all 3 groups and yielded a flowable paste. The accelerator paste consisted of the same amount of powder mixed with resin part 2. Equal masses of the 2 pastes were blended and filled into a  $2 \times 2 \times 25 \text{ mm}^3$  mold. For group 2, the initiator and accelerator monomers are listed as parts 1 and 2, respectively (Table). For group 3, the specimens were heat-cured at  $120^\circ\text{C}$  for 30 min.

A hybrid composite (TPH, Caulk/Dentsply, Milford, DE, USA), containing 78% of silicate particles, about  $0.8 \mu\text{m}$  in diameter, was used as a control and is referred to as hybrid control. The specimens were light-cured (Triad-2000, Dentsply, York, PA, USA) for 2 min. Specimens of an inlay/onlay composite (Concept, Ivoclar, Amherst, NY, USA; designated as inlay/onlay control) were cured in a Concept Heat-Integrated Processor at  $120^\circ\text{C}$  for 10 min under a pressure of 0.6 MPa.

## Measurements of Strength and Ca and $\text{PO}_4$ Release

Flexural strength was measured by a three-point flexural test with a 10-mm span at a crosshead speed of 1 mm/min on a Universal Testing Machine (5500R, MTS, Cary, NC, USA). A NaCl solution (133 mmol/L), buffered with 50 mmol/L HEPES (pH = 7.4;  $37^\circ\text{C}$ ), was used for specimen immersion. The specimens were: (1) stored in an oven at a relative humidity of approximately 50% for 1 day; (2) immersed for 1 day; or (3) immersed for 56 days, all at  $37^\circ\text{C}$ , prior to mechanical testing.

To measure the Ca- $\text{PO}_4$  release, we used the NaCl solution described above. In a previous study, a composite disk of approximately 15.8 mm in diameter and 1.55 mm in thickness was immersed in 100 mL solution (Skrtic *et al.*, 1996a), yielding a composite volume *per* solution of  $3.0 \text{ mm}^3/\text{mL}$  and a surface area/solution of  $4.7 \text{ mm}^2/\text{mL}$ . In the present study, 3 specimens of approximately  $2 \times 2 \times 12 \text{ mm}^3$  were immersed in 50 mL solution, yielding a specimen volume/solution of  $2.9 \text{ mm}^3/\text{mL}$  and a surface area/solution of  $6.2 \text{ mm}^2/\text{mL}$ . The immersion times were: 1 day, 2, 4, 7, 14, 21, 28, 35, 42, 49, and 56 days. At each time, aliquots of 0.5 mL were removed and analyzed for Ca and  $\text{PO}_4$  concentrations with a spectrophotometer (DMS-80 UV-visible, Varian, Palo Alto, CA, USA), according to established standards and calibration methods (Vogel *et al.*, 1983; Skrtic *et al.*, 1996a; Dickens *et al.*, 2003).

We performed two-way ANOVA to detect the significant effects of variables. We performed Tukey’s multiple comparison at  $p = 0.05$  to compare the data.

## RESULTS

TEM (Fig. 1B) showed agglomerated particles, with individual particles having a size of approximately 50 nm (arrows). The XRD pattern (Fig. 1C) had peaks corresponding to DCPA, while the hump suggests that it may be poorly crystalline. The BET measurement yielded a specific surface area of  $18.6 \text{ m}^2/\text{g}$ .

The DCPA-whisker composites before immersion showed decreasing strength with increasing D:W ratio (Fig. 2A). For the composite with HEMA, the flexural strength in MPa at D:W = 1:2 was ( $156 \pm 11$ ), significantly higher than ( $111 \pm 5$ ) at D:W = 2:1 ( $p < 0.05$ ).

For the composite without HEMA, the strength at D:W = 1:2 was ( $148 \pm 9$ ), higher than ( $110 \pm 13$ ) at D:W = 2:1 ( $p < 0.05$ ).

For the heat-cured composite, the strength at D:W = 1:2 was ( $167 \pm 23$ ), not significantly different from ( $137 \pm 18$ ) at D:W = 2:1 ( $p > 0.1$ ). The strength of the heat-cured composite at D:W = 1:2 was higher than ( $103 \pm 32$ ) of the inlay/onlay control ( $p < 0.05$ ). Those of the chemically cured composites at D:W = 1:2, both with and without HEMA, were higher than ( $112 \pm 22$ ) of the hybrid control ( $p < 0.05$ ).

Most composites did not show a significant decrease in strength after 1 day's immersion (Fig. 2B). The heat-cured and the chemically cured nano DCPA-whisker composites without HEMA showed no significant decrease in strength compared with those before immersion ( $p > 0.1$ ). Only the chemically cured composite with HEMA at D:W = 1:2 had a significant strength loss ( $p < 0.05$ ).

After the 56-day immersion (Fig. 2C), the heat-cured composite showed no significant decrease in strength ( $p > 0.1$ ) compared with that of specimens before immersion. The chemically cured DCPA-whisker composites (with and without HEMA) showed significant strength losses ( $p < 0.05$ ).

The ion release increased rapidly with time, then reached a plateau with further increase in time (Fig. 3). The composite with HEMA (D:W = 2:1) had higher release than other composites ( $p < 0.05$ ). For group 1 at 56 days, the total ionic  $\text{PO}_4$  concentration in mmol/L reached ( $1.95 \pm 0.13$ ), ( $0.98 \pm 0.05$ ), and ( $0.43 \pm 0.07$ ), at D:W = 2:1, 1:1, and 1:2, respectively. The corresponding Ca concentrations reached ( $0.68 \pm 0.07$ ), ( $0.38 \pm 0.05$ ), and ( $0.27 \pm 0.01$ ), respectively. Groups 2–3 had similar concentrations; both were slightly lower than those of group 1 ( $p < 0.05$ ).

## DISCUSSION

This study represented the first effort to combine nano-sized Ca- and  $\text{PO}_4$ -releasing fillers with reinforcing fillers in resins. In previous studies, nano-sized inert tantalum-oxide particles (Chan *et al.*, 1999), micron-sized fluoride-releasing fillers (Anusavice *et al.*, 2005), and micron-sized DCPA were used in resins (Dickens *et al.*, 2003). The nano DCPA-whisker composites of the present study possessed flexural strengths similar to those of commercial composites without Ca and  $\text{PO}_4$  release. The reinforcement mechanisms were whiskers pinning and bridging the cracks (Xu *et al.*, 1999, 2002). The whiskers have a tensile strength of about 50 GPa, compared with 2.6 GPa for glass fibers. Fracture toughness is  $> 2 \text{ Mpa}\cdot\text{m}^{1/2}$  for silicon carbide, compared with  $0.7 \text{ Mpa}\cdot\text{m}^{1/2}$  for glass. Hence, the whiskers were more effective in resisting cracks and less likely to be cut through by the cracks, compared with glass fillers in composites.

A previous study used amorphous calcium phosphate (ACP) fillers and developed an ACP remineralizing composite (Skrtec *et al.*, 1996a). When dry specimens without immersion were used, the ACP composite had a three-point flexural strength of ( $47 \pm 5$ ) MPa with unmilled ACP and ( $56 \pm 16$ ) MPa with milled ACP (O'Donnell *et al.*, 2006). In the present study, the nano DCPA-whisker composites for direct-filling had three-point flexural strengths of about 150 MPa before immersion at D:W = 1:2.

After the 56-day immersion, the strength of the chemically cured composite (D:W = 1:2) decreased to ( $104 \pm 6$ ) MPa without HEMA and ( $108 \pm 12$ ) MPa with HEMA. In comparison, a previous composite, with micron-sized DCPA, had a bi-axial flexural strength of 40–60 MPa before immersion; the strength decreased to 10–20 MPa after 90 days of immersion (Dickens *et al.*, 2004). The strength of the ACP composite decreased to 40 MPa after 11 days' immersion (Skrtec *et al.*, 1996a). Hence, the strengths of nano-DCPA-whisker composites were

substantially higher than those of previous Ca- and PO<sub>4</sub>-releasing composites. The nano-silica-whiskers are relatively inert and stable, and previous studies showed that they were strongly bonded with the resin matrix (Xu *et al.*, 2002). Hence, the nano DCPA-whisker composites are expected to have improved long-term durability compared with the previous Ca-PO<sub>4</sub> composites that do not have a stable reinforcement phase. Further studies are needed to investigate the long-term water-aging behavior of the nano DCPA-whisker composites.

It should be noted that a 10-mm span was used in the three-point flexural test, while ISO Specification 4049 (2000) calls for the use of a 20-mm span. To examine any differences, we tested specimens of the hybrid control composite (TPH) using both the 10-mm span and the 20-mm span. The flexural strength values (mean  $\pm$  SD; n = 5) were measured to be (111.7  $\pm$  22.0) MPa and (111.9  $\pm$  14.1) MPa, at 10-mm and 20-mm spans, respectively. Specimens of the heat-cured DCPA-whisker composite (at an intermediate D:W = 1:1) were also tested with both 10-mm and 20-mm spans, yielding (135.7  $\pm$  7.8) MPa and (134.4  $\pm$  17.5) MPa, respectively. Although the strengths with 10-mm and 20-mm spans are nearly the same, future studies should use the 20-mm span, to be consistent with the specification. Another issue is the number of samples: The present study used n = 5, consistent with the ISO Specification 4049, on the three-point flexural test. To examine the effect of n, we tested the heat-cured DCPA-whisker composite (at an intermediate D:W = 1:1) using the 20-mm span. The strength was (134.4  $\pm$  17.5) MPa at n = 5, (136.1  $\pm$  15.1) MPa at n = 10, and (139.4  $\pm$  14.2) MPa at n = 14. While these values were nearly the same, there was a slight decrease in the standard deviation with increasing n.

The ACP composites with HEMA yielded PO<sub>4</sub> concentrations of 0.2–0.7 mmol/L and Ca of 0.3–1.0 mmol/L (Figs. 2–3 in Skrtic *et al.*, 1996a). The nano-DCPA composite with HEMA produced a Ca concentration (0.68 mmol/L) similar to the ACP composites, and a PO<sub>4</sub> concentration (1.95 mmol/L) approximately twice that of ACP composites. Another study on remineralizing Ca-PO<sub>4</sub> composites reported a PO<sub>4</sub> concentration of 0.1 mmol/L and a Ca concentration of 0.5 mmol/L in buffered saline (Dickens *et al.*, 2003).

A reason for the high release from the nano-DCPA composites, even with the non-releasing whiskers serving as part of the fillers, was likely the high surface area of the nano-DCPA, measured to be  $A = 18.6 \text{ m}^2/\text{g}$ . In comparison, in a previous study (Dickens *et al.*, 2003), the DCPA particle size,  $d$ , was 1.1  $\mu\text{m}$ , and the TTCP (tetracalcium phosphate) particle size was 16  $\mu\text{m}$ . The density,  $\rho$ , is 2.89  $\text{g}/\text{cm}^3$  for DCPA and 3.07  $\text{g}/\text{cm}^3$  for TTCP. Hence,  $A = 6/(\rho d) = 1.9 \text{ m}^2/\text{g}$  for DCPA, and  $A = 0.12 \text{ m}^2/\text{g}$  for TTCP, much less than the 18.6  $\text{m}^2/\text{g}$  for the nano DCPA. Smaller particles with a larger surface area may have faster release, resulting in higher ionic concentrations. Previous studies (Skrtic *et al.*, 1996b; Dickens *et al.*, 2003) have shown that when Ca and PO<sub>4</sub> were released, they re-precipitated to form hydroxyapatite outside the composite and inside the tooth lesions, significantly increasing the mineral content of the lesion. The fact that the Ca-PO<sub>4</sub> concentrations from the nano-DCPA-whisker composites matched or exceeded those of previous composites that were shown to remineralize tooth lesions suggests that these nano-DCPA-composites may also be effective remineralizers.

It should be noted that this study focused on developing novel nano-composites with high strength and Ca and PO<sub>4</sub> release, without attempting to simulate the *in vivo* saliva flow and pH changes. Thus, this study demonstrated that the high-strength composites released Ca and PO<sub>4</sub> matching/exceeding the previous remineralizing composites measured by a similar method, without examining the kinetics of the release under *in vivo* conditions. Although this study measured the release up to 56 days, the release is expected to continue after 56 days. The ion concentrations in Fig. 3 plateaued, likely due to the measurement method in which the solution was not changed. Further studies should measure the concentration of the solution at certain time intervals, such as hourly or daily, and replenish the solution with the same volume

of fresh solvent at each time interval. Studies are also needed to investigate the remineralization of enamel and dentin lesions with these high-strength nano DCPA-whisker composites.

In summary, nano DCPA particles were synthesized and incorporated into dental resins for the first time. Significant releases of Ca and PO<sub>4</sub> were obtained from these composites. The addition of nano-silica-fused whiskers resulted in high composite strengths, matching those of commercial stress-bearing, non-releasing composites. Furthermore, the Ca-PO<sub>4</sub> concentrations from the nano-DCPA-whisker composites matched/exceeded those of previous Ca-PO<sub>4</sub> composites that were shown to remineralize tooth lesions, while the flexural strengths of the nano-DCPA-whisker composites were two- to three-fold those of the previous Ca-PO<sub>4</sub> composites. In addition, the processing method of synergistically using calcium phosphate nano-fillers/reinforcement fillers in dental resins may yield new composites with high stress-bearing and caries-inhibiting capabilities, a combination not available in any current dental materials.

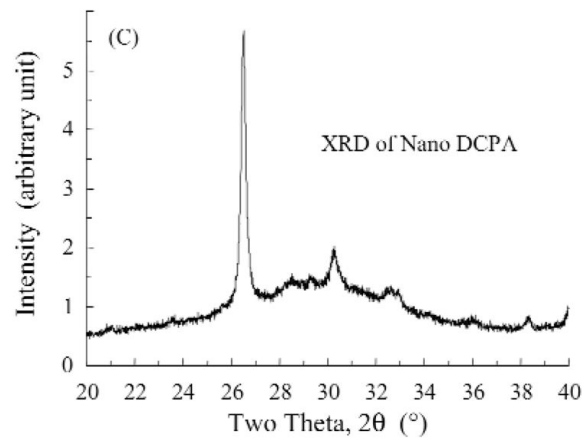
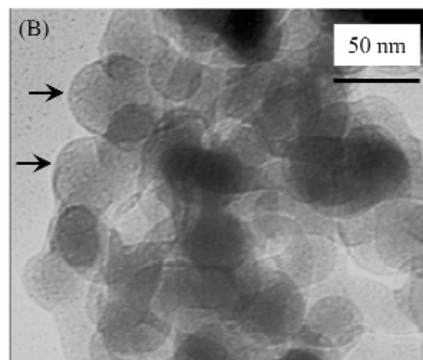
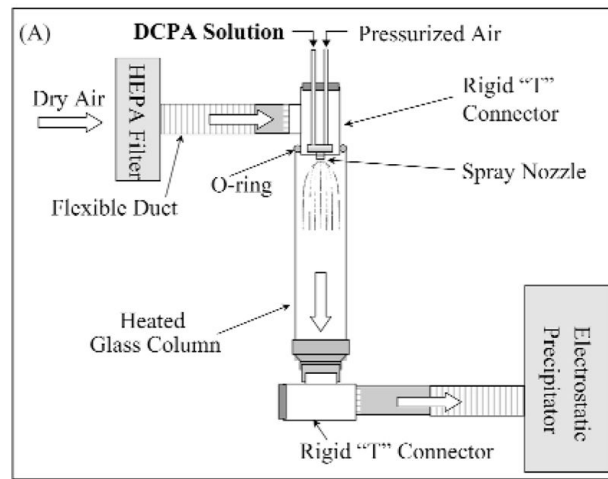
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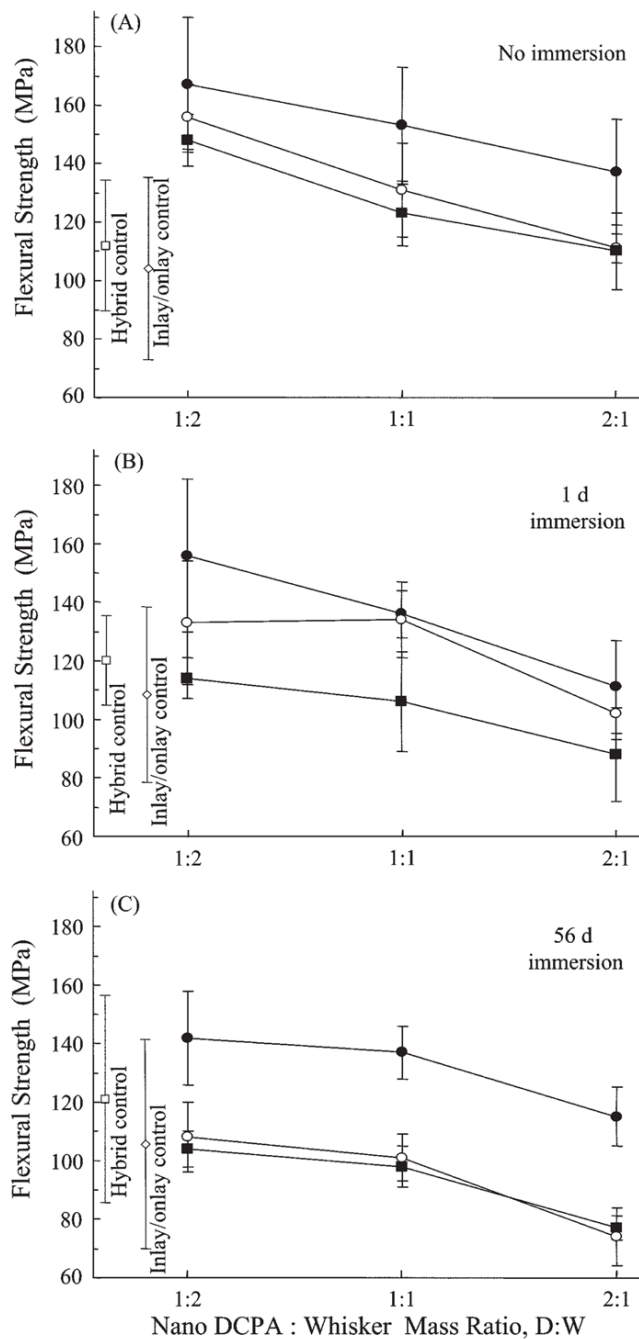
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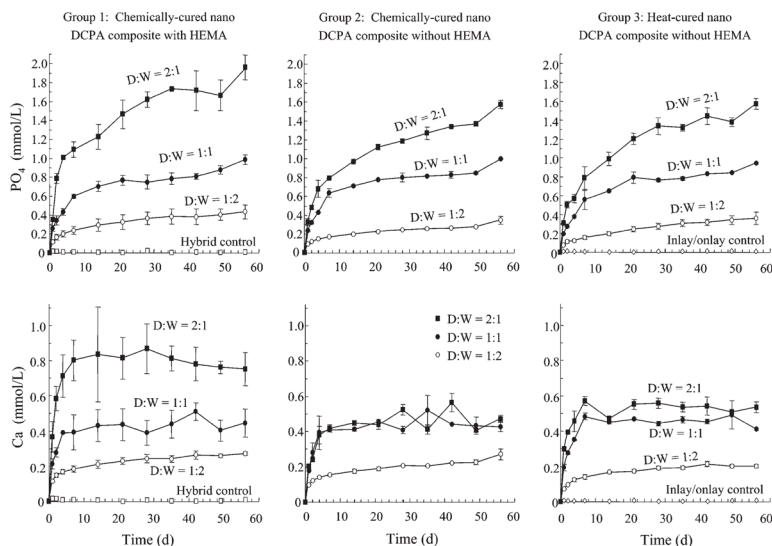
**Figure 1.**

Synthesis of nano DCPA particles. (A) Schematic of the spray-drying apparatus. "HEPA" refers to High Efficiency Particulate Air Filter. The glass column was heated with electrical heating tapes and thermally insulated with a fiberglass tape, reaching an average temperature in the column of  $80^{\circ}\text{C}$ . (B) TEM of nano DCPA particles. Arrows indicate particles about 50 nm in diameter. (C) XRD pattern indicates that the powder was a poorly crystalline DCPA.





**Figure 2.** Composite flexural strength. Heat-cured nano DCPA composite: ●. Chemically cured nano DCPA composite with HEMA: ○. Chemically cured nano DCPA composite without HEMA: ■. Specimens (A) without immersion, (B) after 1 day’s immersion, and (C) after 56 days’ immersion. Each value is the mean of 5 measurements, with the error bar showing 1 standard deviation (SD) (mean ± SD; n = 5). Two-way ANOVA identified significant effects of resin composition and DCPA:whisker ratio ( $p < 0.05$ ), with no significant interaction between the two factors ( $p = 0.86$ ). The 56-day immersion decreased the strength of the chemically cured DCPA-whisker composites, but not the heat-cured DCPA-whisker composites and the controls ( $p > 0.1$ ).



**Figure 3.** PO<sub>4</sub> and Ca release for the 3 groups of composites. Each value is mean ± SD; n = 4. The nano DCPA:whisker mass ratio was designated as D:W. For each group, two-way ANOVA showed significant effects of D:W and immersion time, with a significant interaction between the 2 parameters (P < 0.05). Increasing the D:W ratio significantly increased the PO<sub>4</sub> and Ca concentrations (P < 0.05). At each D:W, increasing the immersion time significantly increased the PO<sub>4</sub> and Ca ion concentrations. The hybrid control and inlay/onlay control had no detectable release.

Table

Matrix Compositions of the 3 Groups of Composites (mass %)\*

	Bis-GMA	TEGDMA	HEMA	BHT	BPO	DHEPT	MEHQ
Group 1	36.475	36.475	25	0.05	2		
part 1	37	37	25			1	
part 2							
Group 2	48.975	48.975		0.05	2		
part 1	49.5	49.5				1	
part 2	48.965	48.965			2		0.07
Group 3							

\* Bis-GMA = bisphenol glycidyl dimethacrylate. TEGDMA = triethylene glycol dimethacrylate. HEMA = 2-hydroxyethyl methacrylate. BHT = 2,6-di-*tert*-butyl-4-methylphenol. BPO = benzoyl peroxide. DHEPT = *N*, *N*-dihydroxyethyl-*p*-toluidine. MEHQ = 4-methoxyphenol. Group 1 used a two-part chemically activated resin system containing HEMA. Group 2 used the two-part chemically activated resin system without HEMA. The purpose was to examine the effects of HEMA on the composite properties. Specimens of Group 3 were heat-cured for indirect applications.