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Long-term mechanical durability of dental nanocomposites containing amorphous calcium phosphate nanoparticles

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Abstract

Half of all dental restorations fail within 10 years, with secondary caries and restoration fracture being the main reasons. Calcium phosphate (CaP) composites can release Ca and PO₄ ions and remineralize tooth lesions. However, there has been no report on their long-term mechanical durability. The objective of this study was to investigate the wear, thermal-cycling, and water-aging of composites containing amorphous calcium phosphate nanoparticles (NACP). NACP of 112-nm and glass particles were used to fabricate four composites: (1) 0% NACP+75% glass; (2) 10% NACP+65% glass; (3) 15% NACP+60% glass; and (4) 20% NACP+50% glass. Flexural strength and elastic modulus of NACP nanocomposites were not degraded by thermal-cycling. Wear depth increased with increasing NACP filler level. Wear depths of NACP nanocomposites after 4×10^5 cycles were within the range for commercial controls. Mechanical properties of all the tested materials decreased with water-aging time. After 2 years, the strengths of NACP nanocomposites were moderately higher than the control composite, and much higher than the resin-modified glass ionomers. The mechanism of strength loss for resin-modified glass ionomer was identified as microcracking and air-bubbles. NACP nanocomposites and control composite were generally free of microcracks and air-bubbles. In conclusion, combining NACP nanoparticles with reinforcement glass particles resulted in novel nanocomposites with long-term mechanical properties higher than those of commercial controls, and wear within the range of commercial controls. These strong long-term properties, plus the Ca-PO₄ ion release and acid-neutralization capability reported earlier, suggest that the new NACP nanocomposites may be promising for stress-bearing and caries-inhibiting restorations.

Keywords

dental nanocomposite; amorphous calcium phosphate; wear; thermal-cycling; long-term water-aging; stress-bearing

INTRODUCTION

There is a need to improve the longevity of composite restorations.¹ Each year, about 200 million dental restorations are placed in the USA.² The popularity and usage of composite restoratives have increased due to their esthetics and direct-filling capability.^{3–9} Their use is supported by the significant advances in resin matrix compositions, improvements in filler particles, and optimization of the polymerization process.^{10–18} Nonetheless, recurrent caries and bulk fracture remain the two main problems for composite restorations.^{19,20} Caries at the restoration margins is a frequent reason for replacement of existing restorations.²¹ It was recognized that half of all dental restorations fail within 10 years, and replacing them consumes nearly 60% of the average dentist's practice time.^{1,22} Replacement dentistry costs \$5 billion in the USA annually.²³ Therefore, it is highly desirable to develop a new class of composites that can combat recurrent caries while sustaining the load-bearing capability.¹

Previous studies have developed calcium phosphate (CaP) composites that can release calcium (Ca) and phosphate (PO₄) ions with remineralization capabilities.^{24–26} Filled with amorphous calcium phosphate (ACP), tetra-calcium phosphate (TTCP), and dicalcium phosphate anhydrous (DCPA) particles with sizes of about 1 to 20 μm, these composites were able to release supersaturating levels of Ca and PO₄ ions and effectively increase the mineral contents of enamel and dentin lesions.^{25,26} CaP composites with mechanical reinforcement achieved higher load-bearing capabilities, without compromising the Ca and PO₄ ion release.²⁷ Although the traditional CaP composites are meritorious, they have relatively low mechanical properties. It was recognized that their strengths were inadequate to make these composites acceptable as bulk restoratives.²⁴ In addition, there has been little study on the long-term mechanical durability of CaP composites, including wear, thermal cycling, and water-aging properties.

ACP composites are promising because ACP is a precursor that forms initially and then transforms to hydroxyapatite [HA: Ca₁₀(PO₄)₆(OH)₂].²⁸ HA is the structural prototype of the major mineral component of teeth and is the final stable product in the precipitation of calcium and phosphate ions in neutral or basic solutions.²⁸ Novel nanoparticles of ACP were recently synthesized and incorporated into a dental composite.²⁹ The high surface area of nanoparticles enabled the composite to release high levels of Ca and PO₄ using a low filler level, thereby making room in the resin for glass fillers as reinforcement. This approach resulted in a photo-cured ACP nanocomposite with Ca and PO₄ release matching those of previous CaP composites, while with mechanical properties nearly twice as high.²⁹ The ACP nanocomposite was “smart” and greatly increased the Ca and PO₄ release at a cariogenic pH of 4, when these ions would be most needed to inhibit caries.²⁹ In addition, the ACP nanocomposite could neutralize the cariogenic pH.³⁰ When placed into a pH 4 solution, the ACP nanocomposite raised the pH to a safe level of 6 which could avoid demineralizing the tooth structure, while commercial restoratives failed to raise the pH.³⁰ However, the long-term mechanical durability of ACP nanocomposite such as wear and water-aging has not been investigated.

The objective of this study was to investigate the wear, thermal cycling, and water-aging behavior of the novel ACP nanocomposite. Three-body wear, thermal cycling, and water immersion for up to 2 years were examined for the ACP nanocomposite versus ACP nanoparticle filler level, in comparison with commercial restorative materials. It was hypothesized that: (1) Increasing the water-aging time will decrease the strength and elastic modulus of all restoratives; (2) Increasing the ACP nanoparticle filler level will decrease the resistance to wear, thermal cycling, and water-aging; and (3) ACP nanocomposite will exceed the long-term mechanical properties and wear resistance of the commercial restoratives.

MATERIALS AND METHODS

Development of nanocomposite containing ACP nanoparticles

ACP ($\text{Ca}_3[\text{PO}_4]_2$) nanoparticles (referred to as NACP) were synthesized via a spray-drying technique.²⁹ Briefly, a solution was prepared using acetic acid glacial (J.T. Baker, Phillipsburg, NJ) and water. Calcium carbonate (CaCO_3 , Fisher, Fair Lawn, NJ) and DCPA (J.T. Baker) were dissolved into this solution to obtain a Ca concentration of 8 mmol/L and a PO_4 concentration of 5.333 mmol/L. This yielded a Ca/P molar ratio of 1.5, the same as that for ACP. This solution was sprayed through a nozzle (PNR, Poughkeepsie, NY) into a chamber with heated air flow.³¹ An electrostatic precipitator (AirQuality, Minneapolis, MN) was connected to the other end of the chamber. The water and volatile acid were evaporated in the heated chamber, and expelled into an exhaust-hood. The dried particles were collected by the electrostatic precipitator. The specific surface area of the particles was measured using multipoint-BET (Autosorb-1, Quantachrome, Boynton Beach, FL). Transmission electron microscopy (TEM, 3010-HREM, JEOL, Peabody, MA) was used to examine the particles. The standard uncertainty for TEM measurement is estimated to be 5%.

To make the composite, both NACP and glass particles were used to achieve Ca and PO_4 release and load-bearing ability. Barium boroaluminosilicate glass particles of a median diameter of 1.4 μm (Caulk/Dentsply, Milford, DE) were silanized with 4% of 3-methacryloxypropyltrimethoxy-silane and 2% *n*-propylamine (mass %, unless otherwise noted). A resin of Bis-GMA (bisphenol glycidyl dimethacrylate) and TEGDMA (triethylene glycol dimethacrylate) at 1:1 mass ratio was rendered light-curable with 0.2% camphorquinone and 0.8% ethyl 4-*N,N*-dimethylaminobenzoate. Four composites were made: (1) 0% NACP + 75% glass; (2) 10% NACP + 65% glass; (3) 15% NACP + 60% glass; and (4) 20% NACP + 50% glass. The total filler level was 75% for (1–3). The filler level for (4) was slightly lower at 70%, since with 20% NACP, the paste was relatively dry if 75% fillers were used. NACP filler levels higher than 20% were not used in order for the NACP nanocomposite to have good mechanical properties. A previous study showed that the Ca and PO_4 release using 10–20% NACP was comparable to previous CaP composites shown to remineralize tooth lesions.²⁹

Three commercial materials were used as comparative controls. A composite with glass nanoparticles of 40 to 200 nm (Heliomolar, Ivoclar Vivadent, Amherst, NY) is referred to as “Composite control.” The fillers were silica and ytterbium-trifluoride at 66.7%. Heliomolar is indicated for Class I and Class II restorations in the posterior region, and Class III–V restorations. A resin-modified glass ionomer (Vitremer, 3M ESPE, St. Paul, MN) is referred to as “RMGI V.” It consisted of fluoroaluminosilicate glass and a light-sensitive, aqueous polyalkenoic acid. Indications include Class III, V and root-caries restoration, Class I and II in primary teeth, and core-buildup. A powder/liquid ratio of 2.5/1 was used (filler mass fraction = 71.4%) according to the manufacturer. Another resin-modified glass ionomer (Ketac Nano, 3M) is referred to as “RMGI K.” It consisted of polycarboxylic acid modified with methacrylate groups and fluoroaluminosilicate glass, with a filler level of 69%. It is a two-part, paste/paste system and dispensed using the Clicker Dispensing System. It is recommended for primary teeth restorations, small Class I restorations, and Class III and Class V restorations.

For thermal-cycling and water-aging tests, each paste was placed into molds of 2 mm $\times$ 2 mm $\times$ 25 mm. Each specimen was photo-cured (Triad 2000, Dentsply, York, PA) for 1 min on each side. For wear testing, the paste was placed into mold cavities of 4 mm diameter and 3 mm depth,³² and photo-cured for 1 min. The specimens were incubated in the humidior at 37°C for 1 d before the treatments as described later.

Thermal-cycling

A computer-controlled two-temperature thermal cycler was used at the Paffenbarger Research Center in the National Institute of Standards and Technology. Two water baths were maintained at temperatures of 5°C and 60°C, respectively. Seven materials were treated with 10^5 thermal cycles: The four experimental composites with NACP filler level of 0, 10, 15, and 20%, and the three commercial controls. Each thermal cycle consisted of 15 s immersion in each water bath and a travel time of 8 s.³³ The two temperatures were chosen to approximate the minimum and maximum temperatures found in the oral cavity. The dwell time of 15 s was chosen based on a previous study.³³ The water baths were constantly stirred with two stirrers (Arrow Engineering, Hillside, NJ). The variation in the temperature of each water bath was within 1°C of the set temperature.

The specimens were first immersed in distilled water at 37°C for 1 d. Then the specimens were divided into two groups. Group 1 was fractured in three-point flexure and designated as “Before thermal cycling.” Group 2 was subjected to thermal cycling as described above, and then fractured in flexure. Group 2 is referred to as “After thermal cycling.”

A three-point flexural test was used to measure the flexural strength and elastic modulus on a computer-controlled Universal Testing Machine at a crosshead-speed of 1 mm/min and a 20-mm span (5500R, MTS, Cary, NC). Flexural strength was calculated as: $S = 3P_{\max}L / (2bh^2)$, where $P_{\max}$ is the fracture load, L is span, b is specimen width and h is thickness. Elastic modulus was calculated as: $E = (P/d)(L^3/[4bh^3])$, where load P divided by displacement d is the slope of the load-displacement curve in the linear elastic region. The standard uncertainty for is estimated to be 3%.

Three-body wear

A four-station wear apparatus (Caulk/Dentsply, Milford, DE) was used to test the wear specimens.³² This machine is similar to that previously reported.³⁴ Briefly, each composite disk (diameter = 4 mm, thickness = 3 mm) was surrounded by a brass ring filled with a water slurry containing 63% by mass of polymethyl methacrylate (PMMA) beads (mean bead size = 44 μm).³² A carbide steel pin with a tip diameter of ~ 3 mm was loaded onto the specimen submerged in the slurry of PMMA beads in each of the four stations. The pin was pressed down against the PMMA particles on the specimen surface and rotated 30°. Upon reaching a maximum load of 76 N, the pin was counter-rotated during unloading and moved upward back to its original position. Each specimen was subjected to 4×10^5 wear cycles, following previous studies.^{32,34} This produced a “dimple-like” wear scar into the specimen surface. To measure the amount of wear, the diameter and depth of each wear scar were measured via a computer-controlled profilometer (Mahr, Cincinnati, OH) equipped with a 5 μm diamond stylus.³² For each worn impression, profilometric tracings were made at intervals of 50 μm in two directions perpendicular to each other, with the unworn surface of the specimen as the baseline. The maximum values in the two perpendicular directions were then averaged to yield the maximum wear scar depth and diameter for each wear scar.³² The standard uncertainty for is estimated to be 3%.

Two-year water-aging

Specimens were immersed in distilled water at 37°C for 0 d, 1 d, 1 month, 3 months, 6 months, 12 months, 18 months, and 24 months. The 0 d group refers to specimens that were incubated at 37°C for 1 d in the humidior without immersion in water, and then tested in flexure. For the immersion specimens, each group of six specimens of the same material was immersed in 200 mL of water in a sealed polyethylene container, following a previous study.³⁵ This constituted a 7×8 full factorial design with seven materials and eight levels of water-aging time. The water was changed once every week. At the end of each time period,

the specimens were fractured using the three-point flexural test to measure flexural strength and elastic modulus. The bars were tested within a few minutes after being taken out of the water and fractured while being wet.

SEM and statistics

Scanning electron microscopy (SEM) was used to examine the specimens after water-aging to understand the mechanisms of degradation. Both the specimen external surfaces and the fractured cross-sectional surfaces were sputter-coated with platinum and palladium, and examined in a SEM (Quanta 200, FEI Company, Hillsboro, OR).

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.

RESULTS

Figure 1 shows the TEM images of NACP from the spray-drying technique. In (A), the small particles had sizes of the order of 10 nm, and the large particles had sizes of about 100–300 nm. Examples of large particles are shown in (B), which appeared to contain small particles. This is more clearly revealed in (C) at a higher magnification, where the arrows indicate small particles that have connected together to form the large particle. The small particles likely fused to form the larger particles in the spray-drying chamber before they were completely dried. Not only did the surface of the large particles consisted of small particles, the interior of the large particles also contained numerous small particles. An example of this is shown in (D). The measurement of fifty randomly selected particles yielded an average particle size of 112 nm.

The thermal cycling results are plotted in Figure 2: (A) Flexural strength and (B) elastic modulus. For the nanocomposite containing NACP, the strength decreased significantly ($p < 0.05$) with increasing the NACP filler level from 0 to 20%, while the glass filler level was decreased from 75 to 50%. The NACP specimens had similar strengths before and after thermal cycling ($p > 0.1$). The NACP nanocomposites had strengths higher than or matching that of the composite control. The NACP nanocomposites had strengths significantly higher than those of RMGI V and RMGI K ($p < 0.05$). For example, flexural strength (mean $\pm$ sd; $n = 6$) of nanocomposite with 20% NACP was (89 ± 13) MPa, slightly higher than (80 ± 14) MPa of composite control, and much higher than (32 ± 2) of RMGI V and (34 ± 2) MPa of RMGI K, all after thermal-cycling. Elastic modulus of these materials showed a similar trend.

The three-body wear results are plotted in Figure 3. In (A), increasing the NACP filler level significantly increased the wear depth ($p < 0.05$). The composite at 0% NACP had a wear depth similar to that of composite control ($p > 0.1$). The composite with 10% NACP had a wear depth similar to that of RMGI V ($p > 0.1$). The wear of the nanocomposite increased at 15 and 20% NACP, but they still had less wear than RMGI K ($p < 0.05$). Wear scar diameter in (B) had a similar trend to that in (A). Nanocomposites with 10–20% NACP had wear scar diameters that were similar to those of RMGI V and RMGI K ($p > 0.1$).

Figure 4 plots the flexural strength of water-aged specimens. The seven materials were separated into two plots for clarity. The strength showed a decreasing trend with increasing immersion time. For example, the nanocomposite with 10% NACP had strength (mean $\pm$ sd; $n = 6$) of (121 ± 10) MPa after 1 d, (98 ± 20) MPa after 3 months, (73 ± 9) MPa after 1 year, and (61 ± 8) MPa after 2 years. These values were significantly different from each other ($p < 0.05$).

The NACP nanocomposites had strengths slightly higher than that of composite control, and much higher than those of the resin-modified glass ionomers. For example, after 2 years, the strengths were (64 ± 10) MPa for 0% NACP, (61 ± 8) MPa for 10% NACP, (50 ± 8) MPa for 15% NACP, (46 ± 9) MPa for 20% NACP, (36 ± 12) MPa for composite control, (15 ± 2) MPa for RMGI V, and (7 ± 3) MPa for RMGI K. Strengths of nanocomposites with 10 and 15% NACP were higher than all three controls at 2 years ($p < 0.05$). The strength of nanocomposite with 20% NACP was similar to that of composite control at 2 years ($p > 0.1$), and both values were higher than those of RMGI V and RMGI K ($p < 0.05$).

In Figure 5, elastic modulus of the nanocomposites decreased with increasing NACP filler level. The decrease in modulus from 1 d to 2 years is relatively small for NACP nanocomposites, as well as for composite control and RMGI V. However, RMGI K had a precipitous drop in modulus from 1 d to 2 years. In addition, while the strength of composite control is higher than that of RMGI V, the modulus of RMGI V is generally higher than composite control except at the 2 year time point. This indicates that a material with a higher strength does not necessarily have a higher modulus.

Figure 6 shows typical SEM micrographs for RMGI K. Both the external surface of the specimen (referred to as “external surface”) and the specimen’s interior cross-section from three-point fracture (referred to as “fracture surface”) were examined. The external surface of RMGI K contained some cracks from 1 d to 2 years, with an example shown in (A) at 1 d. In addition, micron-sized “microcracks” were also present, with an example shown in (B) at 2 years. On the fracture surface, air bubbles with the sizes of the order of $10 \mu\text{m}$ were present from 1 d to 2 years (C). Microcracks were also noticeable in the fracture surface of RMGI K in (D).

Similar cracks were not found in the surfaces of NACP nanocomposites. A typical SEM micrograph is shown in Figure 7 for the nanocomposite with an intermediate 15% NACP. The external surface after 1 d (A) and 2 years of immersion (B) were smooth and generally free of cracks and air bubbles. The fracture surfaces in (C) and (D), at a low and high magnification, respectively, were free of air bubbles and cracks. The surfaces of other NACP nanocomposites appeared similar to those in Figure 7. The external surfaces and fracture surfaces of the composite control (not included) were also similar to Figure 7 and free of cracks and air bubbles.

DISCUSSION

This study investigated the long-term durability of ACP nanocomposites for the first time. Thermal cycling for 10^5 cycles, wear for 4×10^5 cycles, and water-aging for up to 2 years were tested. CaP composites are promising restoratives to combat recurrent caries because of their release of Ca and PO_4 ions and remineralizing capability.^{25,26} However, their long-term mechanical properties and durability are unknown. There has been no report on CaP composite behavior in thermal cycling, wear, and long-term water-aging. The restoration’s resistance to thermal cycling is important. For example, ice water and other cold drinks may approach a temperature of 0°C , while hot soup and tea may surpass 60°C . The difference in thermal expansion between the restoration and the tooth may contribute to restoration-tooth debonding and microleakage. Furthermore, for the resin composite, there are internal stresses due to the thermal expansion difference between the resin matrix and the filler particles. The thermal coefficient of expansion is about 8 to $12 \times 10^{-6}/^\circ\text{C}$ for glass and ceramic fillers, and $76 \times 10^{-6}/^\circ\text{C}$ for acrylic resin.^{36,37} During heating, the filler particle tends to expand less than the resin matrix. During cooling, the resin matrix tends to shrink more than the filler. Therefore, there are cyclic tensile and compressive stresses inside the composite. This study measured the mechanical properties of composites before and after

10^5 thermal-cycles between 5 and 60°C. For a simply estimate, assume 50 such thermal-cycles per day in the oral cavity. This would indicate that it takes about 5.5 years to complete 10^5 thermal-cycles. This study found that none of the seven materials showed any significant decrease in strength due to thermal cycling. Only RMGI V showed a small decrease in elastic modulus, with no loss in strength. This indicates that an oral temperature range of 5–60°C was relatively safe for these materials. In addition, the strengths of NACP composites were slightly higher than that of the commercial composite control, and much higher than the resin-modified glass ionomers.

Wear is another important property for dental restoratives. Wear resistance is needed for the functionality of restoratives to maintain contour and occlusion. Hence, occlusal wear resistance is a major requirement for the longevity of load-bearing restorations.^{38–43} Wear testing methods were developed to simulate *in vivo* wear conditions.^{5,10,40,41,43} Three-body wear using artificial food slurries was shown to produce wear that corresponded well with the clinical wear results.^{40,41,43,44} Regarding the correlation between *in vitro* wear and clinical wear, a previous study⁴¹ used the same type of wear machine as that of this study, and compared the results with *in vivo* data. They found that the 4×10^5 cycles of *in vitro* wear values agreed with the *in vivo* wear values over a 3-year period. Hence, this test yields relatively long-term wear properties of the materials. In this study, the NACP nanocomposites had wear depth and width that were within the range of wear of the commercial materials tested. It should be noted that the NACP nanocomposites had other advantages, including the ability to increase the Ca and PO₄ release at cariogenic pH to combat caries,²⁹ and to neutralize acids and raise the pH to a safe level, while the commercial materials failed to neutralize the acids.³⁰

Long-term water-aging is another important property for dental restoratives.^{6–8,45} Water and saliva attack could weaken the composite due to the degradation of filler particles,^{35,46} deterioration of the polymer matrix,⁴⁷ and debonding of the filler-resin interfaces.^{6,48,49} This study showed that increasing the NACP filler level decreased the strength and elastic modulus of the nanocomposite during water-aging. However, due the silanized glass particle reinforcement, the mechanical properties of the NACP nanocomposite were higher than those of the commercial materials after 2 years of water-aging. It is interesting to note that the strength and elastic modulus were proportional to the glass filler level in the NACP composite, with higher glass filler levels yielding higher mechanical properties. Therefore, the composite design method should include both ion-releasing fillers and stable reinforcement fillers, to achieve both caries-inhibiting and load-bearing capabilities.

An important approach to inhibiting caries and promoting remineralization is the development of CaP-resin composites.^{24,25} These composites released Ca and PO₄ ions to supersaturating levels with respect to tooth mineral, could protect teeth from demineralization, and could regenerate lost tooth mineral *in vitro*.^{25,26} Using NACP with a high surface area, high levels of Ca and PO₄ release could be achieved at low NACP filler levels of 10–20%. The NACP particles had a specific surface area of ~18 m²/g.²⁹ In comparison, the specific surface area for traditional ACP particles was about 0.5 m²/g. Therefore, the nanocomposite could reach Ca and PO₄ releases comparable to those of previous CaP composites, while using a lower filler level. This left room in the resin for glass fillers, so that the NACP composite relied on glass fillers, not CaP fillers, for mechanical reinforcement. A previous study reported the flexural strength for a traditional ACP composite to be 30–40 MPa after 14 d of immersion.²⁴ It should be noted that traditional ACP composites and CaP composites in previous studies did not contain glass fillers.^{24–26} Using CaP fillers with sizes of several microns to tens of microns which had much less surface area than nanoparticles, the resins were fully filled with CaP particles to have sufficient Ca and PO₄ ion release. In comparison, the new NACP nanocomposites with

glass particles had much higher flexural strengths of 70–110 MPa after 90 d immersion, and 50–70 MPa after 2 years of immersion.

The commercial composite control (Heliomolar) is indicated for Class I and II posterior restorations, Class III and IV anterior restorations and Class V restorations. Indications for Vitremer include Class III, V and root-caries restoration, Class I and II in primary teeth, and core-buildup. The NACP nanocomposites had mechanical properties higher than the controls after thermal cycling and 2-year water-aging, and wear resistance within the range of the controls. Hence, the NACP nanocomposites may also be suitable for the aforementioned applications, with the added benefits of Ca and PO₄ release and acid neutralization capability to inhibit caries.^{29,30} Other potential applications of the NACP nanocomposites include treatments where complete removal of caries tissue is contra-indicated, in teeth where carious lesions are beginning to occur, and for patients at high risk for dental caries including those receiving radiation treatments or with dry mouth. Further studies should optimize the NACP nanocomposite composition and investigate its *in situ* performance.

SUMMARY

This study investigated the long-term mechanical durability of novel nanocomposites containing amorphous calcium phosphate nanoparticles for the first time. Thermal cycling, three-body wear, and water-aging for up to 2 years were tested. Thermal cycling between 5 and 60°C for 10⁵ cycles did not significantly degrade the flexural strength and elastic modulus of the nanocomposites. The NACP nanocomposite mechanical properties were slightly higher than that of a commercial control composite, and much higher than those of resin-modified glass ionomers. Increasing the NACP filler level decreased the mechanical properties and increased the amount of wear. The wear depth and width of the NACP nanocomposites after 4 × 10⁵ cycles were within the range of the commercial controls. Increasing the water-aging time from 1 d to 2 years decreased the mechanical properties of all the seven materials tested. At 2 years, the strengths of NACP nanocomposites were moderately higher than the control composite, and much higher than resin-modified glass ionomers. Microcracking and air bubbles were found in a commercial control. The NACP nanoparticles had a high surface area to contribute to the ion release, enabling the use of a low NACP filler level, thus making room in the resin for 50–65% of glass reinforcement particles. This combination of NACP and glass fillers yielded good mechanical durability for the nanocomposite. The strong long-term properties, together with the Ca and PO₄ release and acid neutralization capacity reported previously, make the NACP nanocomposite promising for stress-bearing and caries-inhibiting restorations.

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FIGURE 1.

Typical TEM micrographs of nanoparticles of amorphous calcium phosphate (NACP). (A) Low magnification. Arrows indicate examples of a small particles (about 10 nm) and larger particles (about 100–300 nm). (B) Large particles at an intermediate magnification. (C) Higher magnification. Arrows indicate small particles that are visible that have fused at the surface of a large particle. (D) The interior of the large particles also consisted of numerous small particles (arrows). TEM measurement of 50 random particles resulted in an average particle size of 112 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 2.

Thermal cycling results: (A) Flexural strength and (B) elastic modulus. Each value is the mean of six measurement, with the error bar showing one standard deviation (mean $\pm$ sd; $n = 6$). The thermal cycler consisted of two water baths at 5 and 60°C, respectively. Both before and after thermal-cycling, the strengths of NACP nanocomposites were moderately higher than that of the control composite, and much higher than those of the resin-modified glass ionomer controls. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 3.

Three-body wear after 4×10^5 cycles: (A) Wear scar depth and (B) wear scar diameter. Each value is mean $\pm$ sd; $n = 6$. The wear of NACP nanocomposite showed an increasing trend with increasing NACP filler level. The wear depth and width of the NACP nanocomposites were within the range of the wear for the commercial controls. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 4.

Flexural strength after water-aging for 2 years. Each value is mean $\pm$ sd; $n = 6$. The seven materials are separated into (A) and (B) for clarity. The strengths of nanocomposites with 10 and 15% NACP were significantly higher than all three controls at 2 years ($p < 0.05$). The strength of nanocomposite with 20% NACP was not significantly different from that of composite control at 2 years ($p > 0.1$), and both values were higher than those of RMGI V and RMGI K ($p < 0.05$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 5.

Elastic modulus of the water-aged materials. The NACP nanocomposite is plotted as a function of NACP filler level. The three controls are also included. The seven materials are separated into (A) and (B) for clarity. Each value is mean $\pm$ sd; $n = 6$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 6.

SEM examination of water-aged RMGI K: (A, B) External surfaces of the specimens after 1 d and 2 years of immersion, respectively. (C, D) Fracture surfaces at 2 years at low and high magnifications, respectively. Some cracks were observed in the external surfaces of the specimens (A). Microcracks were present at a higher magnification (B). (C) Air bubbles and (D) microcracks were found in the fracture surfaces (arrows). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FIGURE 7.

SEM examination of water-aged NACP nanocomposite, with an intermediate 15% NACP filler level. (A, B) External surfaces of the specimens after 1 d and 2 years of immersion, respectively. (C, D) Fracture surfaces at 2 years at low and high magnifications, respectively. The nanocomposite appeared to be dense and solid. The external surfaces and fracture surfaces of the nanocomposite were generally free of cracks and air bubbles.