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Nanocomposite containing CaF₂ nanoparticles: Thermal cycling, wear and long-term water-aging

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Abstract

Objectives—Fluoride (F) releasing dental restoratives are promising to promote remineralization and combat caries. The objectives of this study were to develop nanocomposite containing calcium fluoride nanoparticles (nCaF₂), and to investigate the long-term mechanical durability including wear, thermal-cycling and long-term water-aging behavior.

Methods—Two types of fillers were used: nCaF₂ with a diameter of 53 nm, and glass particles of 1.4 μm. Four composites were fabricated with fillers of: (1) 0% nCaF₂ + 65% glass; (2) 10% nCaF₂ + 55% glass; (3) 20% nCaF₂ + 45% glass; (4) 30% nCaF₂ + 35% glass. Three commercial materials were also tested. Specimens were subjected to thermal-cycling between 5 °C and 60 °C for 10⁵ cycles, three-body wear for 4×10⁵ cycles, and water-aging for 2 years.

Results—After thermal-cycling, the nCaF₂ nanocomposites had flexural strengths in the range of 100–150 MPa, five times higher than the 20–30 MPa for resin-modified glass ionomer (RMGI). The wear scar depth showed an increasing trend with increasing nCaF₂ filler level. Wear of nCaF₂ nanocomposites was within the range of wear for commercial controls. Water-aging decreased the strength of all materials. At 2 years, flexural strength was 94 MPa for nanocomposite with 10% nCaF₂, 60 MPa with 20% nCaF₂, and 48 MPa with 30% nCaF₂. They are 3–6 fold higher than the 15 MPa for RMGI (*p* < 0.05). SEM revealed air bubbles and cracks in a RMGI, while composite control and nCaF₂ nanocomposites appeared dense and solid.

Significance—Combining nCaF₂ with glass particles yielded nanocomposites with long-term mechanical properties that were comparable to those of a commercial composite with little F release, and much better than those of RMGI controls. These strong long-term properties, together with their F release being comparable to RMGI as previously reported, indicate that the nCaF₂ nanocomposites are promising for load-bearing and caries-inhibiting restorations.

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Keywords

Dental nanocomposite; CaF₂ nanoparticles; mechanical properties; thermal cycling; three-body wear; water-aging

1. Introduction

Fluoride (F)-releasing restoratives are frequently studied because the F ions could increase the dissolution resistance of the tooth structure, enhance remineralization and hinder demineralization [1-5]. Efforts have been made to develop and improve glass ionomers, resin-modified glass ionomers, and compomers [6-10]. One advantage of these materials is that F ions could be incorporated into the tooth to form fluoroapatite or F-enriched hydroxyapatite, both with lower solubility than hydroxyapatite. Another advantage is that while F ions had little effect on *Streptococcus mutans* viability, high F ion concentrations significantly reduced the acid production of biofilms [11]. These properties are important in view of the fact that recurrent caries is a major reason for restoration failure [12-14]. The replacement of failed restorations accounts for 50-70% of all restorations that are placed [15,16]. Replacement dentistry costs \$5 billion annually in the U.S. [17]. F-releasing restoratives are promising to addressing this problem by promoting remineralization and inhibiting microbial growth and metabolism [9].

While useful for low-load-bearing restorations, glass ionomer cements do not have sufficient mechanical properties to be used in large-load-bearing restorations. It was predicted that “the most intractable problem (for glass ionomers) is likely to be lack of strength and toughness” [18]. Resin-modified glass ionomers were developed with improved mechanical strength, less moisture sensitivity, and better clinical handling properties [19]. However, the mechanical enhancement was rather limited. For example, when traditional and resin-modified glass ionomers were immersed in water for 12 months, it was shown that the microhardness was not enhanced with the addition of resins [20]. Efforts are being made to improve the F-releasing materials [3,5,8,21-25]. Resin composites possess good mechanical properties and wear resistance [26-34]. Therefore, one approach to improving the load-bearing capability of F-releasing restorations is to incorporate F-releasing fillers in resin composites.

Calcium fluoride nanoparticles (nCaF₂) were recently synthesized via a spray-drying technique [35] and incorporated into resin composite [24]. The composite containing 20% nCaF₂ had a cumulative F release of 2.34 mmol/L at 10 weeks [24]. The initial F release rate was 2 μg/(h·cm²), and the sustained release-rate at 10 weeks was 0.29 μg/(h·cm²). These values matched or exceeded the reported releases of traditional and resin-modified glass ionomers [24]. Immersion in solutions of pH 4 to 7 yielded similar strengths for the nCaF₂ nanocomposites, which were significantly higher than the strengths of commercial F-releasing controls [36]. In addition, the nCaF₂ nanocomposite was smart and greatly increased the F release at cariogenic low pH when these ions are most needed to inhibit caries [36]. However, the long-term mechanical durability of the nCaF₂ nanocomposites has not been reported.

The objective of this study was to investigate the thermal-cycling, three-body wear, and 2-year water-aging behavior of the nCaF₂ nanocomposites vs. nCaF₂ filler level. It was hypothesized that: (1) Increasing the nCaF₂ filler level will decrease the mechanical durability of the nanocomposite and increase the wear amount; (2) The nCaF₂ nanocomposites will have less wear than the commercial controls; (3) nCaF₂

nanocomposites will possess higher mechanical properties than commercial controls after thermal-cycling or water-aging for two years.

2. Materials and Methods

2.1 Fabrication of nCaF₂ nanocomposites

A spray-drying apparatus described recently was used to synthesize the nCaF₂ [24,35]. Briefly, a two-liquid nozzle (ViscoMist, Lechler, St. Charles, IL) was employed to allow two solutions to be mixed at the time of atomization. Calcium hydroxide, Ca(OH)₂, was used to make the calcium solution [24,35]. Ammonium fluoride, NH₄F, was used to prepare the fluoride solution. The two-liquid nozzle sprayed the solution into the heated chamber of the spray-dryer. The reaction of Ca(OH)₂ and NH₄F led to: $\text{Ca(OH)}_2 + 2\text{NH}_4\text{F} \rightarrow \text{CaF}_2 + 2\text{NH}_3\uparrow + 2\text{H}_2\text{O}\uparrow$. The CaF₂ nanoparticles were collected via an electrostatic precipitator (MistBuster, Air Quality Eng., Minneapolis, MN). The NH₃ and H₂O vapors were removed with the air flow. The nanopowder was confirmed to be CaF₂ by X-ray diffraction in a previous study [24]. The nanopowder was dried in air overnight at 110 °C, and multipoint BET particle surface area analyses were performed (AUTOSORB-1, Quantachrome, Boynton Beach, FL) with ultra-high-purity nitrogen as the adsorbate gas and liquid nitrogen as the cryogen. Transmission electron microscopy (TEM, 3010-HREM, JEOL, Peabody, MA) was used to examine the particles.

A monomer consisting of 48.975% Bis-GMA (bisphenol glycidyl dimethacrylate), 48.975% TEGDMA (triethylene glycol dimethacrylate), 0.05% 2,6-di-*tert*-butyl-4-methylphenol, and 2% benzoyl peroxide formed part I, the initiator, of a two-part chemically-activated resin [24]. Part II, the accelerator resin, consisted of 49.5% Bis-GMA, 49.5% TEGDMA, and 1.0% *N,N*-dihydroxyethyl-*p*-toluidine. The two-part chemically-activated system was used because the nCaF₂ paste was relatively opaque. Besides nCaF₂ fillers, barium boroaluminosilicate glass particles of a median size of 1.4 μm (Caulk/Dentsply, Milford, DE) were used as a co-filler for mechanical reinforcement. Glass particles were silanized with 4% (all mass%, unless otherwise noted) 3-methacryloxypropyltrimethoxysilane and 2% *n*-propylamine [37]. Four composites were fabricated with the following fillers: (1) 0% nCaF₂ + 65% glass; (2) 10% nCaF₂ + 55% glass; (3) 20% nCaF₂ + 45% glass; (4) 30% nCaF₂ + 35% glass. nCaF₂ filler levels of 40% or higher were not used because a previous study showed that the composite with 20% nCaF₂ had F release comparable to that of a resin-modified glass ionomer. In addition, it is desirable to have at least 35% of glass fillers for reinforcement. Each resin was mixed with the filler particles, and then equal masses of paste I and paste II were mixed to form the chemically-cured composite. For thermal-cycling and water-aging, the mold dimensions were 2 mm × 2 mm × 25 mm. For wear, the mold cavity had a 4-mm diameter and 3-mm depth [38]. Specimens were incubated at 37 °C in a humidior for 1 d prior to treatments as described in subsequent sections.

In addition, three commercial materials were tested as comparative controls. A composite with glass nanoparticles of 40-200 nm (Heliomolar, Ivoclar Vivadent, Amherst, NY) is referred to as “Composite control”. The fillers were silica and ytterbium-trifluoride with a filler level of 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-carries 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 V restorations. The specimens were photo-cured (Triad 2000, Dentsply, York, PA) for 1 min on each open side. Specimens were incubated in a humidior at 37 °C for 1 d prior to the treatments described below.

Thermal-cycling test—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. The seven materials were treated with 10^5 thermal cycles. Each cycle consisted of 15 seconds (s) immersion in each water bath and a travel time of 8 s [39]. The two temperatures were chosen to approximate the minimum and maximum temperatures found in the oral cavity. The water baths were constantly stirred with stirrers, and the variation in the temperature of each water bath was within 1 °C of the set temperature. All specimens for this test were first immersed in distilled water at 37 °C for 1 d. Then the specimens were divided into two groups. Group 1 had no thermal-cycling and was fractured in three-point flexure. Group 1 is designated as “Before thermal-cycling”. Group 2 was subjected to thermal-cycling as described above, and then fractured in three-point flexure. Group 2 is referred to as “After thermal-cycling”. The specimens of both groups were tested in three-point flexure in the same manner.

Flexural testing—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.

Three-body wear test—Wear was tested using a four-station wear apparatus (Caulk/Dentsply, Milford, DE) [38], similar to that previously described [40]. Each composite disk (diameter = 4 mm, thickness = 3 mm) was surrounded by a brass ring filled with a water slurry containing 63% of polymethyl methacrylate (PMMA) beads (mean size = 44 μm). A carbide steel pin with a tip diameter of 3 mm was loaded onto the specimen, which was submerged in the slurry of PMMA beads in each of the four stations. The pin was pressed down against the PMMA beads 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 [38,40]. This type of wear produced a “dimple-like” wear scar into the specimen surface. 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. 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 the maximum diameter for each wear scar [38,40].

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 a humidior without immersion 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 [41]. The water was changed once every week. At the end of each time period, the specimens were fractured using the aforementioned three-point flexural test to

measure the flexural strength and elastic modulus. The immersed 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 treatment. Both the specimen external surfaces and the fractured cross-sections 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

TEM images of the nCaF₂ are shown in Fig. 1. Examples of nCaF₂ are shown in Fig. 1A with particle sizes of the order of 10 nm. Some larger particles were present with an example in Fig. 1B, having sizes of about 100-300 nm. These particle sizes are consistent with the BET measurement which obtained a specific surface area of 35.5 m²/g, yielding a particle size of 53 nm. The larger particles appeared to have been formed by numerous fine particles, which likely were fused together in the spray-drying chamber before the fine particles were fully dried. An example of a mixture of fine particles and large particles are shown in Fig. 1C.

Fig. 2 plots the thermal-cycling results. In Fig. 2A, the flexural strength of nCaF₂ nanocomposite showed a decreasing trend with increasing nCaF₂ filler level, because the glass filler level was decreasing from 65% to 35%. The strengths of composites with 0%, 10% and 20% of nCaF₂ were not significantly different from each other ($p > 0.1$). The strength at 30% nCaF₂ was significantly lower than that at 0% nCaF₂ ($p < 0.05$). Composite control had a strength similar to that of the nanocomposite with 30% nCaF₂ ($p > 0.1$). The strength of composite control was significantly lower than those at 0%, 10% and 20% of nCaF₂ ($p < 0.05$). All nCaF₂ nanocomposites had strengths in the range of 100-150 MPa, about 5 times higher than the 20-30 MPa for the commercial resin-modified glass ionomers.

Most materials showed no significant difference in strength before and after thermal-cycling. Only the nanocomposite with 30% nCaF₂ and RMGI K had a slightly higher strength after thermal-cycling. The same is true for elastic modulus in Fig. 2B, where in general the materials had similar moduli before and after thermal-cycling. The nCaF₂ nanocomposites had moduli that were within the range of the moduli of commercial controls.

Fig. 3 plots the three-body wear of nCaF₂ nanocomposite vs. filler level, along with the controls. Both the wear scar depth in Fig. 3A and wear width in Fig. 3B showed an increasing trend with decreasing the glass filler level. The composite with 0% and 10% nCaF₂ had wear depths similar to that of composite control ($p > 0.1$). All the nCaF₂ nanocomposites had wear depths that were not significantly different from that of RMGI V ($p > 0.1$). RMGI K had higher wear than all the other materials ($p < 0.05$). The wear width showed a similar trend, with RMGI V having a similar wear width to those of the nCaF₂ nanocomposites ($p > 0.1$).

The 2-year water-aging results are plotted in Fig. 4A-B for flexural strength, and Fig. 4C-D for elastic modulus. The strength showed a generally decreasing trend with increasing water-aging time. For example, the nanocomposite with 20% nCaF₂ had strength (mean \pm sd; $n =$

6) of (125 ± 16) MPa without immersion, (109 ± 17) MPa after 6 months of immersion, (91 ± 23) MPa after 1 year of immersion, and (60 ± 13) MPa after 2 years of immersion.

At each immersion time period, the nCaF₂ nanocomposites had strengths slightly higher than composite control, and much higher than RMGI V and RMGI K. At 2 years, flexural strengths for the seven materials were: (92 ± 22) MPa for 0% nCaF₂, (94 ± 14) MPa for 10% nCaF₂, (60 ± 13) MPa for 20% nCaF₂, (48 ± 8) MPa for 30% nCaF₂, (36 ± 12) MPa for composite control, (15 ± 2) MPa for RMGI V, and (7 ± 3) MPa for RMGI K. The elastic moduli are plotted in Fig. 4C and Fig. 4D. In water-aging from 1 d to 2 years, the percentage of decrease in modulus is smaller than the percentage of decrease in strength. In addition, nCaF₂ nanocomposites, composite control, and RMGI V had smaller modulus losses than RMGI K.

SEM was used to examine the external surface and the fracture surface (cross-section) of the water-aged specimens. Typical SEM micrographs are shown in Fig. 5 for RMGI K. Cracks were found in the external surface of RMGI K specimens from 1 d to 2 years. An example of these cracks (arrows) is shown in Fig. 5A at 2 years. Voids that appeared to be air bubbles were seen in the fracture surfaces of RMGI K from 1 d to 2 years, with an example in Fig. 5B at 1 d. The fracture surface of RMGI K contained cracks, with examples (arrows) in Fig. 5C at 2 years.

Fig. 6 shows SEM micrographs for composite control. In Fig. 6A at 1 d, the external surface appeared relatively smooth and free of cracks such as those in Fig. 5. The external surface of composite control was similar from 1 d to 2 years. The fracture surface was free of air bubbles, and an example is shown in Fig. 6B. However, occasional flaws or irregular voids were found in the fracture surface of composite control, with an example shown in Fig. 6C at 2 years.

SEM images for the nCaF₂ nanocomposite are shown in Fig. 7, at an intermediate nCaF₂ filler level of 20%. The nCaF₂ nanocomposite appeared similar to composite control, with smooth and crack-free surfaces. A typical external surface is shown in Fig. 7A at 1 d. There was no obvious change in the surfaces from 1 d to 2 years. The fracture surface of nCaF₂ nanocomposite appeared dense and solid, without air bubbles or voids. Examples of fracture surfaces are shown in Fig. 7B at 1 d, and Fig. 7C at 2 years. No cracks or signs of matrix disintegration were found in the nCaF₂ nanocomposite with immersion from 1 d to 2 years.

DISCUSSION

F-releasing materials are a promising class of dental restoratives because the F ions can enrich neighboring tooth structure and render them more resistant to decay [1-5], and can hinder the metabolic activity of acidogenic biofilms [11]. Therefore, extensive studies have been performed to develop and improve F-releasing restoratives [3,5-8,10,22,25]. Glass ionomers and resin-modified glass ionomers have relatively lower mechanical properties, and hence are limited to low-load-bearing restorations and in patients with a high caries risk. F-releasing composites have better load-bearing capabilities, but their F release was minimal. The new nCaF₂ nanocomposites have the rare combination of high levels of F release and yet being mechanically strong. In the present study, the long-term mechanical durability of nCaF₂ nanocomposites, including thermal-cycling, wear, and water-aging, was investigated for the first time.

Recent studies showed that the new nCaF₂ nanocomposites had F release that matched or exceeded those of commercial F-releasing restoratives [24]. The long-term F release rates at 70-84 d were $1.13 \mu\text{g}/(\text{cm}^2\cdot\text{day})$ and $0.50 \mu\text{g}/(\text{cm}^2\cdot\text{day})$ for nanocomposite containing 30% and 20% nCaF₂, respectively, similar to the $0.65 \mu\text{g}/(\text{cm}^2\cdot\text{day})$ of RMGI V [36]. These F

release rates were two orders of magnitude higher than the $0.006 \mu\text{g}/(\text{cm}^2\cdot\text{day})$ for the F-releasing composite control (Heliomolar). The previous study showed that the strengths of nCaF₂ nanocomposites were nearly 3-fold that of resin-modified glass ionomer, and were comparable to, or higher than, that of a commercial composite with little F-release [36]. However, the previous studies did not investigate the long-term mechanical durability of the nCaF₂ nanocomposites.

Thermal-cycling could create internal stresses in a composite which could potentially degrade the composite over time. Daily drinks such as ice water and icy soda could approach a temperature of 0 °C. Hot soup, tea and coffee could surpass a temperature of 60 °C. For a composite in a tooth cavity, the difference in thermal expansion between the restoration and the surrounding tooth structure may contribute to restoration-tooth debonding and microleakage. In addition, for the composite itself, there are internal stresses due to thermal expansion differences between the resin and the filler particles. For example, 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 [42,43]. With increasing temperature, the filler particle would expand less than the resin matrix. With decreasing temperature, the resin matrix would shrink more than the filler. In the present study, the seven materials were subjected to 10^5 thermal-cycles between 5 °C and 60 °C. None of the seven materials showed any significant decrease in mechanical properties due to thermal-cycling; only RMGI V showed a small decrease in elastic modulus. Hence, the internal stresses due to thermal-cycling between a relatively small temperature range of 5-60 °C did not cause significant damage to these restorative materials. In addition, dwelling at a temperature of 60 °C could cause further polymerization and increase the degree of conversion for the resins. Therefore, there were two competing factors in thermal-cycling: The water immersion and cyclic thermal stresses that could degrade the material and decrease the mechanical properties; and the high temperature of 60 °C that could improve the degree of conversion and enhance the mechanical properties. Fig. 2 indeed showed that several materials had slightly higher strength and modulus after thermal-cycling. However, the changes in either direction were relatively small. In general, the results in Fig. 2 demonstrated that the flexural strengths of the novel nCaF₂ nanocomposites moderately exceeded that of the commercial composite control, and were 3-4 fold that of resin-modified glass ionomers, both before and after thermal-cycling.

Oral wear is another key property for restorations [28,40,44-48]. Wear is directly related to the functionality of restorative materials, and excessive wear and material loss would cause the restoration to lose contour and be out of occlusion. Efforts were made to improve the occlusal wear resistance of restorative materials [38,45,47]. In addition, wear testing methods were developed to simulate *in vivo* wear conditions [28,40,44,46,48]. It was demonstrated that three-body wear using artificial food slurries yielded wear amounts that corresponded well with the clinical wear results [40,44,45]. Regarding the correlation between these *in vitro* wear values and clinical wear, a previous study [40] used the same type of wear machine as that of the present 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 three-year period. The nCaF₂ nanocomposites had wear depth and width that were slightly larger than the composite control, matched those of RMGI V, and were significantly less than those of RMGI K. Hence, the wear of CaF₂ nanocomposites was within the range of wear of the commercial controls.

Dental composites *in vivo* function in a wet oral environment which could degrade the restorations [31,34,49-51]. It is established that composites could be weakened by long-term water-aging, which could degrade the fillers [41,49], soften the resin due to the plasticizing action of water [50], and cause hydrolytic breakdown of the interfaces between the fillers

and the resin matrix [20,31,50]. Because the present study focused on nCaF₂ nanocomposites, a commercial nanocomposite with F release and a nano-structured resin-modified glass ionomer cement were selected as controls; it should be noted that other F-releasing composites are also available which may possess different properties. A recent study examined three commercial composites which showed F release and recharge when aged in deionized water and lactic acid [10]. During immersion for 3 months, the F-releasing composites had significantly higher mechanical properties than glass ionomer cements [10], consistent with the results of the present study. These results confirm the importance of glass filler reinforcement. Incorporating glass reinforcement particles in the nCaF₂ composite effectively increased the mechanical properties. Indeed, at 2 years, the strength of nCaF₂ nanocomposite was significantly higher with higher glass filler levels (Fig. 4A). Furthermore, the mechanical properties of glass particle-reinforced nCaF₂ nanocomposites were significantly higher than those of the resin-modified glass ionomers, which did not have stable glass particles for reinforcement.

The results in Figs. 2-4 suggest that it is beneficial to incorporate both F-releasing fillers and non-releasing glass fillers in the same restorative material, in order to obtain good mechanical properties for the F-releasing restorative. The key is that the restorative should not rely on fillers that release ions to provide mechanical properties. Instead, the restorative should rely on strong and non-releasing fillers for mechanical properties. The dilemma, however, is that the restorative that contain sufficient amounts of releasing fillers does not have enough room in the matrix to incorporate reinforcing fillers. On the other hand, restoratives that contain sufficient amounts of reinforcing fillers do not have much room in the matrix to accommodate F-releasing fillers. This results in restoratives that have either high levels of F release but are mechanically weak, or high mechanical properties but with little F release. To date, the material that has high mechanical properties and high F release is yet to be developed. Fortunately, the new generation of nanoparticles with ion release may provide the solution to achieving both high levels of F release and strong and long-lasting mechanical properties in the same composite.

This is because the small size of nCaF₂ with a high surface area can contribute to a high level of ion release even at a low filler level in the composite. A recent study showed that the Ca and PO₄ ion release were greatly increased when the particle size was reduced from 0.88 μm to 0.11 μm, while the type of resin and the filler level were kept the same [37]. The nCaF₂ of the present study had a mean diameter of 53 nm, and a specific surface area $A = 35.5 \text{ m}^2/\text{g}$. For the purpose of illustration, assume a traditional particle size $d = 1 \text{ μm}$. With the CaF₂ density $\rho = 3.18 \text{ g/cm}^3$, the specific surface area would be $A = 6/(d \rho) = 1.9 \text{ m}^2/\text{g}$ for the traditional CaF₂ particles with 1 μm in size. Hence, compared to traditional micron-sized particles, the nCaF₂ had a specific surface area that was nearly 20-fold larger. This large surface area allowed the use of relatively low filler levels of 10-30% for nCaF₂ to achieve F release that was comparable to resin-modified glass ionomers [36]. As a result, there is significant room left in the resin matrix for reinforcement glass fillers to increase the mechanical properties. The present study showed that, indeed, the higher the glass filler level, the higher the strength during thermal-cycling and two-year water-aging, and the better the wear resistance. With the incorporation of both nCaF₂ and glass fillers, the nanocomposite relied on the glass fillers, not the nCaF₂ fillers, for mechanical reinforcement. The nCaF₂ paste was relatively opaque with a greyish color, possibly caused by metal ions in the spray-drying process. Further effort is needed to improve the spray-drying technique and develop esthetic nanoparticles capable of high levels of F release. In addition, further study should optimize the nCaF₂ nanocomposite structure. For example, while using 20% nCaF₂, the glass filler level could possibly be increased from the current 45% to 50% or 55%, to further improve the long-term durability for load-bearing restorations, while maintaining the F release to inhibit caries.

Summary

Two types of fillers (nCaF₂ nanoparticles with a diameter of 53 nm, and glass particles with a size of 1.4 μm) were incorporated into a resin to develop F-releasing nanocomposite with load-bearing capabilities. The rationale was to address the need that restoratives with high levels of F release are mechanically weak, restoratives with large load-bearing capabilities had no or little F release, and the restorative with both high F-release and high mechanical properties is not available. The nanocomposites of this study exhibited strong mechanical durability when tested in thermal-cycling, wear, and water-aging for 2 years. Thermal-cycling between 5 °C and 60 °C for 10⁵ cycles did not degrade the flexural strength and elastic modulus of the nanocomposites. Three-body wear depth and width of the nCaF₂ nanocomposites were within the range of the commercial controls. Increasing the immersion time from 1 d to 2 years decreased the mechanical properties of all the seven materials tested. At 2 years, the strengths of nCaF₂ nanocomposites were moderately higher than that of the control composite, and 3-6 fold higher than those of resin-modified glass ionomers. Recent studies showed that nCaF₂ nanocomposite with 20-30% nCaF₂ had F release rates comparable to that of a resin-modified glass ionomer. The strong long-term mechanical properties and high F release suggest that the new nCaF₂ nanocomposites are promising for stress-bearing and caries-inhibiting restorations.

Supplementary Material

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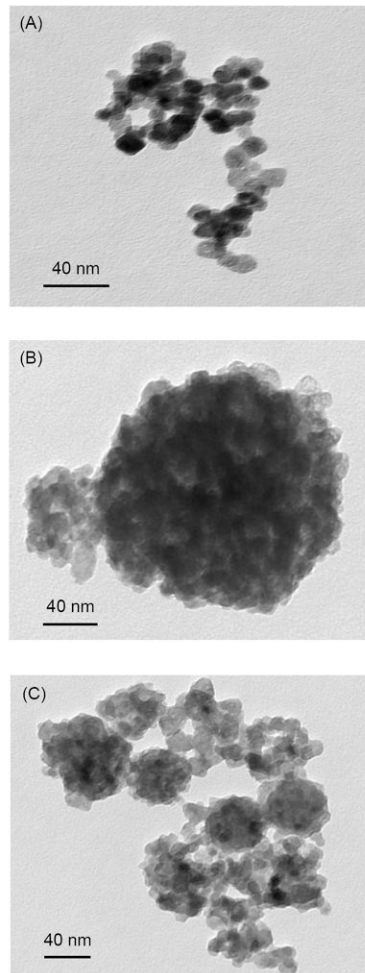


Figure 1. TEM images of CaF₂ nanoparticles (nCaF₂) synthesized using the spray-drying technique and collected via the electrostatic precipitator. (A) Fine nCaF₂ particles. (B) Relatively large nCaF₂ particles. (C) A mixture of fine and large particles.

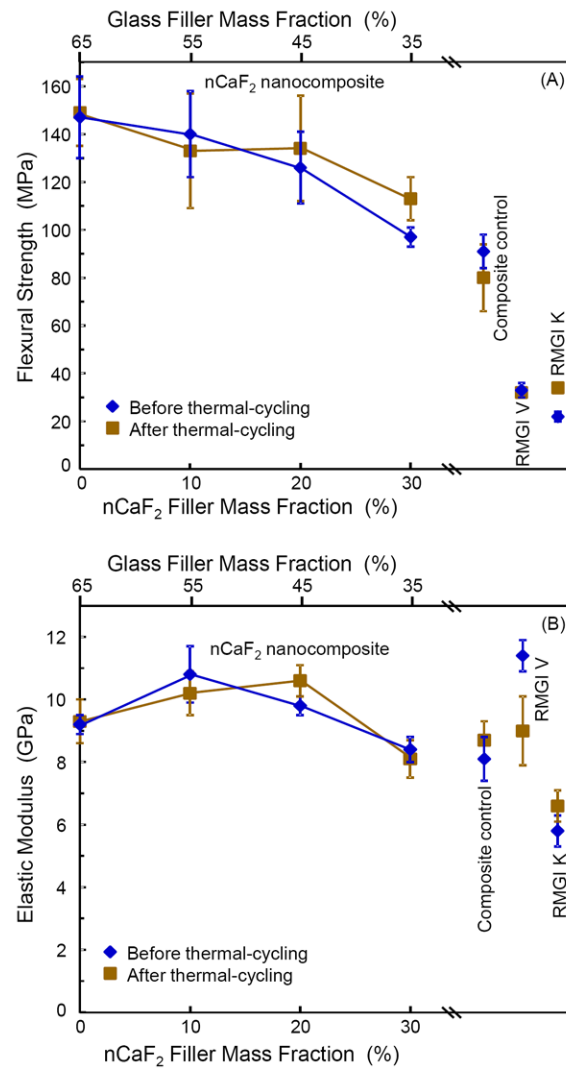


Figure 2. Mechanical properties before and after thermal-cycling. (A) Flexural strength, and (B) elastic modulus. In each plot, the upper axis lists the glass filler level in the nCaF₂ nanocomposite, and the lower axis lists the corresponding nCaF₂ filler level. Values for the three commercial controls are included near the right axis. Each value is the mean of six measurements, with the error bar showing one standard deviation (mean \pm sd; n = 6).

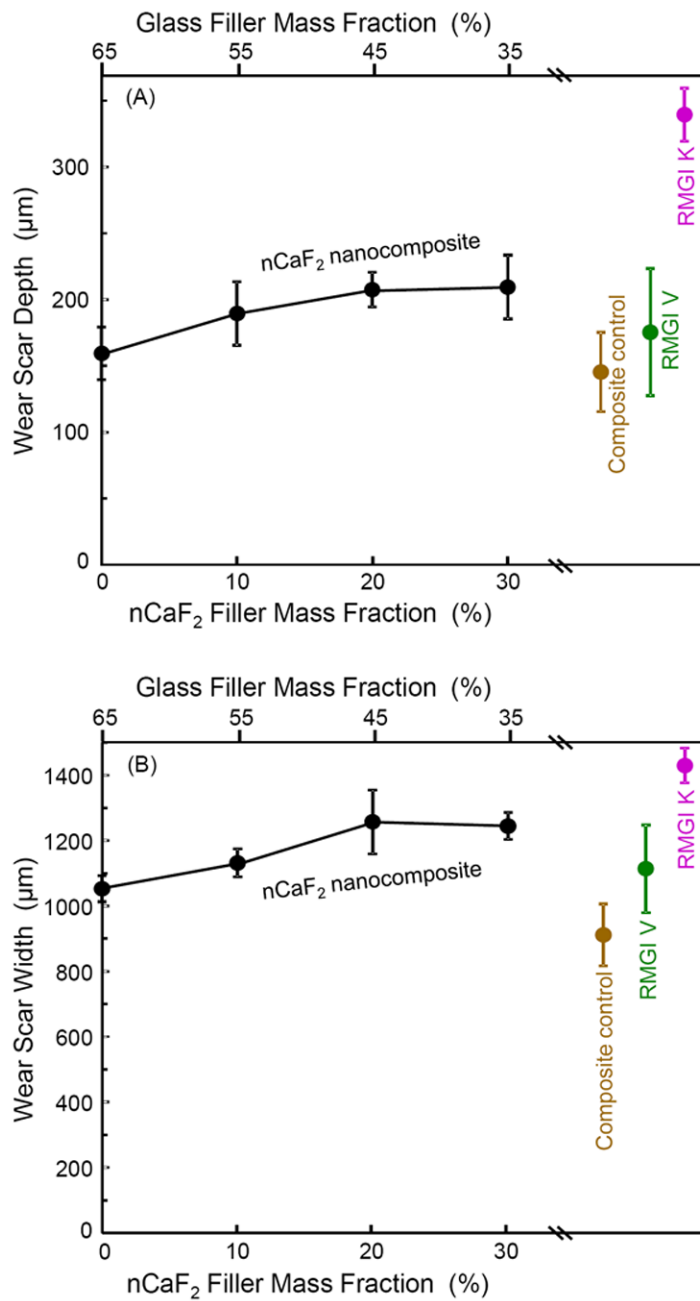


Figure 3.

Three-body wear of nCaF₂ nanocomposites and the controls. Wear produced a dimple-like scar into the composite surface. (A) Wear scar depth, and (B) wear scar width. In each plot, the upper axis lists the glass filler level in the nCaF₂ nanocomposite, and the lower axis lists the corresponding nCaF₂ filler level. Each value is mean \pm sd; n = 6.

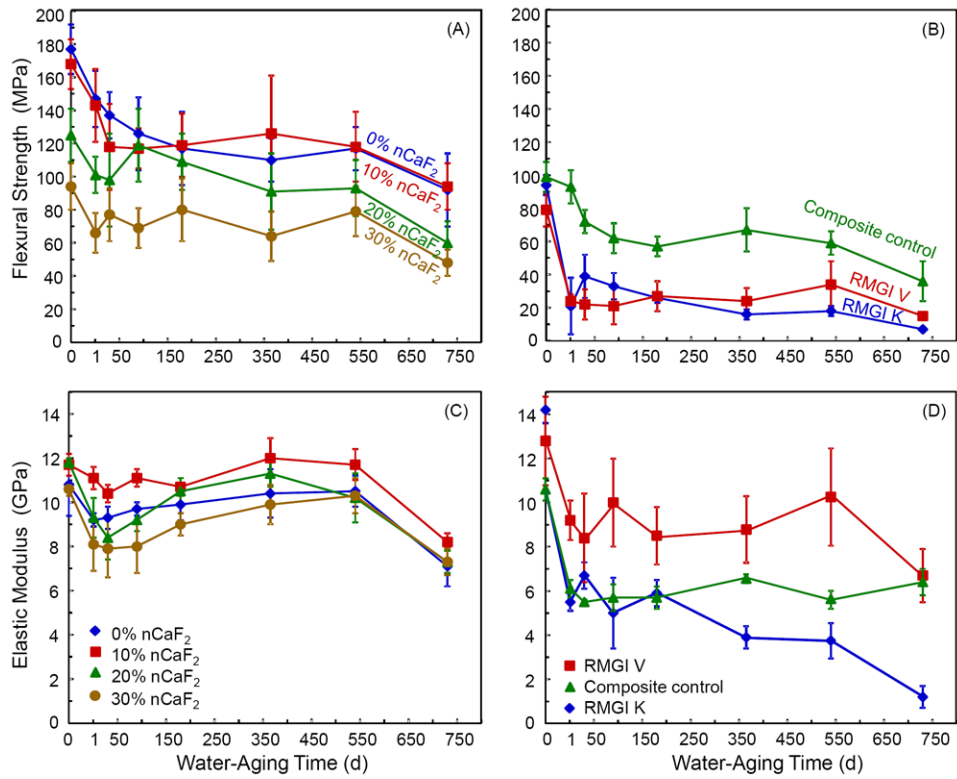


Figure 4. Long-term water-aging results of the nCaF₂ nanocomposites and the control materials. Specimens were immersed in water at 37 °C for up to two years. (A and B) Flexural strength, and (C and D) elastic modulus. For each property, the seven materials were separated into two plots for clarity. Each value is mean ± sd; n = 6.

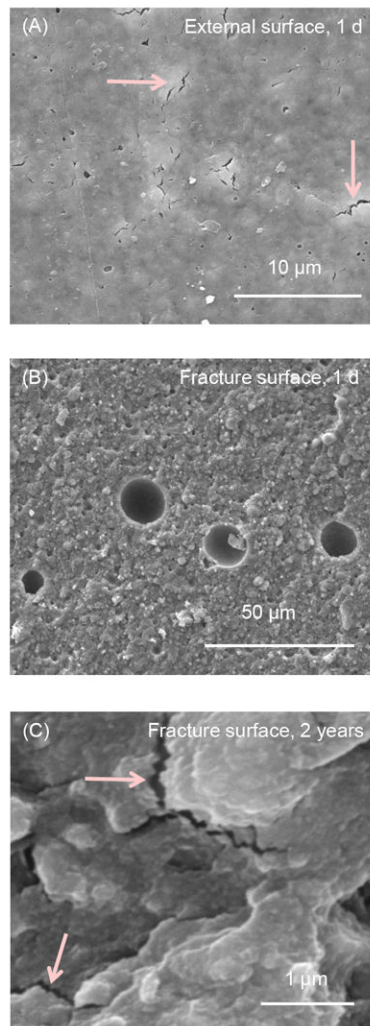


Figure 5. SEM micrographs for RMGI K. The specimen surface was referred to as the “external surface”. The interior of the specimen opened by three-point flexure is referred to as the “fracture surface”. (A) External surface after 2 years of immersion showed the existence of cracks. (B) Fracture surface at 1 d had voids that appeared to be air bubbles. (C) Fracture surface at 2 years had cracks, with examples indicated by the arrows.

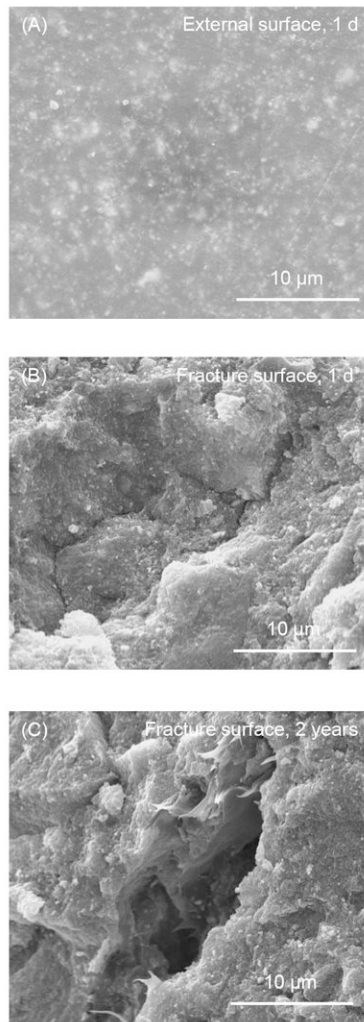


Figure 6. SEM micrographs for the composite control. (A) The external surface at 1 d was relatively smooth and free of cracks. Immersion for 2 years did not noticeably change the appearance of composite control. (B) Fracture surface at 2 years was free of the circular air bubbles. (C) Occasional flaws were noticed in the fracture surface of composite control. This example is in a specimen after 2 years of water-aging.

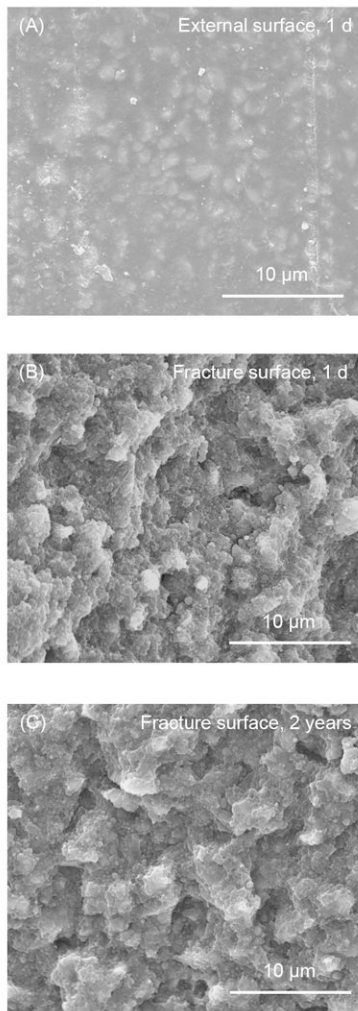


Figure 7. SEM micrographs for nCaF₂ nanocomposites, at an intermediate nCaF₂ filler level of 20%. External and fracture surfaces for the nCaF₂ nanocomposites were similar to those of the composite control. (A) The external surfaces were smooth and crack-free from 1 d to 2 years. This example is for a specimen immersed for 1 d. Fracture surfaces of nCaF₂ nanocomposite appeared dense and solid, and were generally free of air bubbles and other voids, with examples shown in (B) at 1 d, and (C) at 2 years.