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Nanoparticle Loading Level and Properties of Experimental Hybrid Resin Luting Agents

Luciano V. Habekost, DDS, MS,[1] Guilherme B. Camacho, DDS, PhD,[1] Giana S. Lima, DDS, MS, PhD,[1] Fabrício A. Ogliari, DDS, MS, PhD,[2] Glória B. Cubas, DDS, MS,[1] & Rafael R. Moraes, DDS, MS, PhD[1]

[1]School of Dentistry, Federal University of Pelotas, Pelotas, Brazil
[2]Materials Engineering School, Federal University of Pelotas, Pelotas, Brazil

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Correspondence
Rafael R. Moraes, School of Dentistry, Federal University of Pelotas, Rua Goncalves Chaves 457, Pelotas RS 96015560, Brazil.
E-mail: moraesrr@gmail.com

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Abstract

Purpose: This study investigated the influence of nanoparticle loading level on properties of experimental hybrid resin luting agents.
Materials and Methods: Silanated 2-μm barium borosilicate glass microparticles and 7-nm silica nanoparticles were used. Five materials were obtained by loading a photocurable Bis-GMA/TEGDMA co-monomer with a total mass fraction of 60% inorganic fillers. The mass fraction of nanoparticles was set at 0% (control), 1% (G1), 2.5% (G2.5), 5% (G5), or 10% (G10). The properties evaluated were flexural strength (σ) and modulus (E_f), Knoop hardness number (KHN), and film thickness (FT). Dispersion/interaction of the particles with the resin phase was assessed by scanning electron microscopy (SEM). Data were submitted to statistical analysis (5%).
Results: For σ, $G1 > G2.5 = G5 = G10$, and $\text{control} > G10$. For E_f, $G2.5 > \text{control} = G1 > G5 > G10$. For KHN, $G5 = G10 > \text{control} = G1 = G2.5$. For FT, $G10 = G5 > \text{control} = G1$, and $G10 > G2.5$. Incorporation of nanoparticles was associated with observation of clusters in the SEM analysis. The clusters were more frequent for higher nanoparticle loadings.
Conclusion: Modest incorporation of nanoparticles may improve the properties of resin luting materials. Nanofiller mass fractions above 2.5% should, however, be avoided because they may be detrimental to the properties of the resin luting agents.

The use of resin luting agents to lute ceramic restorations has been associated with a strengthening effect of the restorative material.[1,2] The higher the mechanical properties of the luting agent, the higher the fracture resistance of the luted ceramic.[2,3] Dental resin luting agents consist of a resin matrix reinforced with inorganic particles; a coupling agent mediates the bond between these two phases.[4] The introduction of well-dispersed inorganic particles into the resin phase has been shown to greatly influence the performance of polymer composites.[5] The dispersed phase is designed to enhance the modulus of the softer polymer phase and usually consists of glass or ceramic particles of different compositions and sizes.

Nanostructured dental composites were introduced in an endeavor to enhance their esthetic properties by increasing the retention of polish and gloss while having equivalent or improved physical properties compared with traditional hybrid composites.[6] The shape, amount, and size of the particles reinforcing the composite might affect its properties. Decreasing the interparticle space is a key to improving the mechanical strength by increasing the protection of the softer resin matrix. Reduced interparticle spacing may be achieved by either decreasing the size of the particles or increasing the volume fraction of fillers.[7,8] The advantage of hybrid materials is that the introduction of nanoparticles may fill the areas between larger microparticles, allowing for accommodation of higher filler levels without drastically interfering with the handling properties of the composite.

Due to their small size and high surface area, nanoparticles have been also associated with the formation of clusters within the mixed composite.[9] Depending on the connective status of the fillers within the clusters, these may either increase the mechanical properties or act as stress-concentrating areas, decreasing the polymer strength.[10-12] Therefore, the literature presents contrasting results regarding the properties of composites modified with nanoparticles; these have shown either similar,[13-15] slightly better,[13] or worse results,[15,16] compared with traditional hybrid materials. The effect of nanoparticle incorporation into resin luting agents, however, is still unknown.

The aim of this study was to investigate the influence of the nanoparticle fraction incorporated in dental hybrid resin luting agents on key properties of these materials. The null hypotheses tested were: (i) the properties of the resin luting agents would be independent of the nanoparticle fraction, and (ii) there would be no differences in the ultrastructural features of luting agents obtained with different nanoparticle fractions.

Materials and methods

Formulation of the experimental resin luting agents

A model dimethacrylate co-monomer blend based on a 1:1 mass ratio of 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl]propane (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) (Esstech Inc., Essington, PA) was loaded with a 0.4% mass fraction of camphorquinone (Esstech), 0.8% mass fraction of ethyl 4-dimethylamino benzoate (Sigma-Aldrich, St. Louis, MO), and 0.1% mass fraction of butylated hydroxytoluene (Sigma-Aldrich) as radical scavenger. All chemicals were used as received.

Barium borosilicate glass microparticles (2 μm average size) (Esstech) and silica nanoparticles (7 nm average size) (Aerosil 380; Degussa, Frankfurt am Main, Germany) were coated with 5 wt% of the silane coupling agent 3-(trimethoxysilyl)propyl methacrylate (Sigma-Aldrich) diluted in a 96% ethanol-water solution. The particles soaked into the solution and were left to dry at 80°C for 24 hours to assure complete solvent removal. After storage, the fillers were sieved through a 150-μm sieve. Five resin luting agents were obtained by loading the model blend with a mass fraction of 60% inorganic fillers. From the total mass of 60%, the mass fraction of nanoparticles was set at 0% (control), 1%, 2.5%, 5%, or 10%. The particles were incorporated by intensive manual mixing followed by mechanical stirring with a motorized mixer. To assure the adequate dispersion of the filler system, the materials were ultrasonicated for 1 hour.

Flexural strength and modulus

Flexural tests were performed using bar specimens with dimensions of 12 × 2 × 2 mm (8 mm span width).[17] The resin luting agent was placed into the stainless steel/glass mold, covered with a Mylar strip, and photoactivated using two irradiations of 40 seconds on each side. A 3-point bending test was carried out 24 hours after irradiation using a mechanical testing machine (DL500; EMIC, São José dos Pinhais, Brazil), at a 0.5 mm/min cross-head speed. Flexural strength (σ) and flexural modulus (E_f) were calculated from the load-displacement trace. For each group, 18 specimens were tested.

Hardness

The materials were placed into cylindrical metal molds (5 mm inner diameter × 2 mm thick), covered with a Mylar strip and photoactivated for 40 seconds on each surface. After 24 hours, the specimens were wet-ground with 800-, 1000-, 1200-, and 1500-grit SiC abrasive papers. Three readings were performed on each specimen per group through a microindenter (FM-700; Future-Tech, Kawasaki, Japan), under a 25-g load and a 5-second dwell time. The Knoop hardness number (kgf/mm^2) for each specimen was recorded as the average of the three indentations. Five specimens were tested for each luting agent.

Film thickness

Two optically flat square glass plates, each 5 mm thick, and having a contact surface area of 200 mm^2 were used. The combined thickness of the glass plates stacked in contact was measured (reading A) with a digital caliper (MDC-Lite; Mitutoyo, Suzano, Brazil), accurate to 0.001 mm. Then, 0.1 ml of resin luting agent was placed centrally between the plates, and a constant load of 150 N was carefully applied vertically and centrally via the top plate, for 180 seconds. After this period, light irradiation was performed for 40 seconds to stabilize the specimen. The combined thickness of the two glass plates and the luting agent film was measured (reading B). Film thickness was recorded as the difference between reading B and reading A. Five specimens were tested for each luting agent.

Scanning electron microscopy (SEM) analysis

To observe the dispersion and interaction of the filler particles within the resin phase, cylindrical specimens (5 mm diameter × 1 mm thick) were embedded in epoxy resin and wet-polished with 600-, 1200-, 1500-, 2000-, and 2500-grit SiC papers and with 3, 1, 0.25, and 0.1 μm diamond polishing suspensions. The specimens were coated with gold and the polished surfaces examined by SEM (SSX-550; Shimadzu, Kyoto, Japan) at 15 kV.

Statistical analysis

Data for flexural strength, hardness, and film thickness were submitted to one-way ANOVA. Elastic modulus data did not achieve the homocedasticity criteria and were submitted to ANOVA on Ranks. All pairwise multiple comparison procedures were carried out by the Student-Newman-Keuls' method. Regression analyses were used to investigate the relationship between the gradual addition of nanoparticles and each property. A 0.05 significance level was set for all analyses.

Results

Results for all evaluations are shown in Table 1. The power of the performed statistical tests was $\geq$0.964. Nonlinear regression plots are shown in Figure 1. The material with 1% nanoparticles showed significantly higher flexural strength than luting agents with 2.5%, 5%, and 10% nanoparticles ($p \leq 0.046$). The control luting agent showed significantly higher flexural strength as compared with the 10% nanoparticle material ($p = 0.049$). The regression model for flexural strength showed a peak behavior ($R^2 = 0.997$), although it was not significant ($p = 0.329$). The luting agent with 2.5% nanoparticles showed significantly higher flexural modulus compared with all other luting agents ($p < 0.05$); similar results were observed for the luting agents with 0% and 1% nanoparticles ($p > 0.05$), both showing a significantly higher modulus than the luting agents with 5% and 10% nanoparticles ($p < 0.05$). The material with 10% nanoparticles showed significantly lower modulus than

Table 1 Means (SD) for flexural strength (σ), flexural modulus (E_f), hardness (Knoop hardness number [KHN]), and film thickness (FT)

	Nanoparticle loading (mass fraction)*				
	0%	1%	2.5%	5%	10%
σ, MPa	144 (18) ^{AB}	153 (9) ^{A}	140 (21) ^{BC}	132 (14) ^{BC}	131 (13) ^{C}
E_f, GPa	1.90 (0.4) ^{B}	1.85 (0.1) ^{B}	2.00 (0.2) ^{A}	1.77 (0.2) ^{C}	1.62 (0.1) ^{D}
KHN, kgf/mm^2	35.4 (1.7) ^{B}	37.7 (4.2) ^{B}	35.9 (2.2) ^{B}	44.2 (4.2) ^{A}	42.6 (3.6) ^{A}
FT, μm	25.2 (8.6) ^{C}	26.4 (8.1) ^{C}	33.0 (10.7) ^{BC}	39.8 (5.5) ^{AB}	48.8 (7.2) ^{A}

*The total mass fraction of inorganic fillers (nano and microparticles) was 60%.
Distinct letters in a row indicate significant differences for nanoparticle loading ($p < 0.05$).

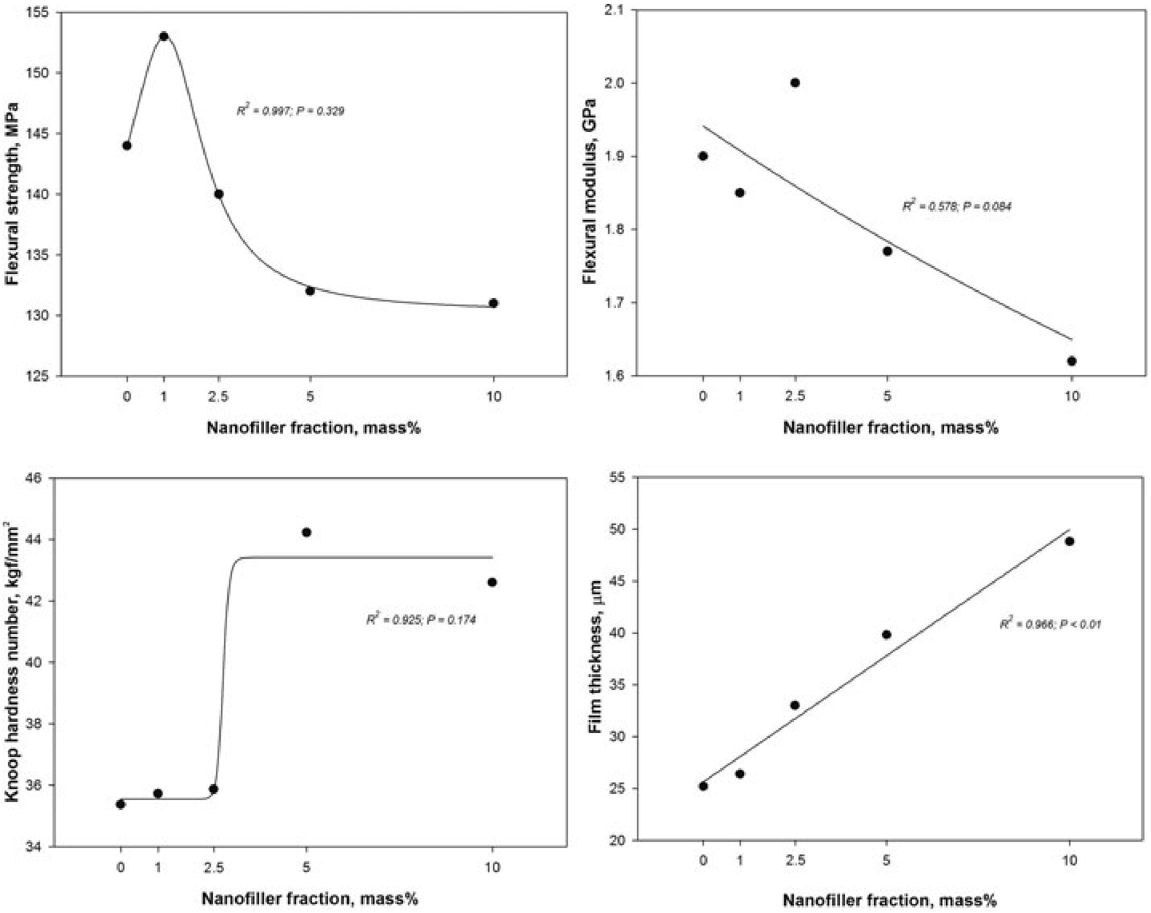

Figure 1 Nonlinear regression plots used to investigate the relationship between the gradual addition of nanoparticles and each property.

all the other luting agents ($p < 0.05$). The regression curve followed rational behavior ($R^2 = 0.578$), but the model was not statistically significant ($p = 0.084$).

The hardness of the luting agents with 5% and 10% nanoparticles was significantly higher compared with all the other luting agents ($p \leq 0.031$). Materials with 0%, 1%, and 2.5% nanoparticles showed similar hardness ($p \geq 0.389$). The regression curve followed sigmoidal behavior ($R^2 = 0.925$), but the model was not statistically significant ($p = 0.174$). For film thickness, materials with 0% and 1% nanoparticles showed significantly lower values compared with the luting agents with 5% and 10% ($p \leq 0.048$), whereas the luting agent containing 2.5% nanoparticles showed a significantly lower value than the luting agent with 10% ($p \leq 0.05$). The regression model followed linear significant behavior ($R^2 = 0.966$; $p < 0.01$), showing an increase in film thickness associated with the increase in the fraction of nanoparticles incorporated into the luting agent.

Representative SEM images of the luting agent surfaces are shown in Figure 2. The incorporation of nanoparticles was associated with the observation of nanoparticle clusters, which showed as darker areas surrounded by microparticles (examples are indicated by asterisks in Figs 2B–E). No clustering was

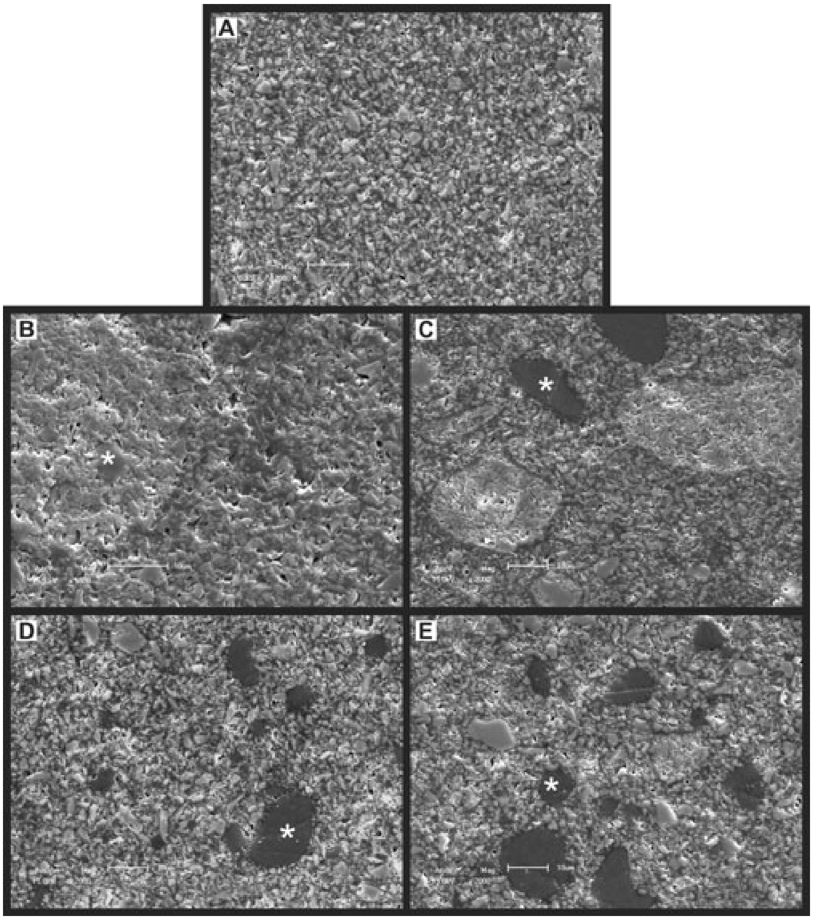

Figure 2 Representative scanning electron microscopy images of polished luting agent surfaces with different nanoparticle loadings: (A) 0%; (B) 1%; (C) 2.5%; (D) 5%; and (E) 10%. The incorporation of nanoparticles was associated with the observation of nanoparticle clusters (darker areas surrounded by microparticles as indicated by asterisks in B to E). No clustering was detected in the control luting agent (A). The clusters were more frequently observed for materials with higher nanoparticle loading levels.

detected in the control luting agent (Fig 2A). The clusters were more frequently observed for materials with higher nanoparticle loads.

Discussion

The first null hypothesis was rejected because the nanoparticle fraction had a significant influence on the properties of the resin luting agents. Incorporation of 1% nanoparticles increased the flexural strength, whereas dispersion of up to 2.5% nanoparticles improved the flexural modulus; however, low nanofiller fractions had a discreet impact on the flexural properties of the luting agents, probably because of the large proportion of microparticles exerting the main influence on the mechanical properties of the hybrid materials. Beyond 2.5%, the incorporation of nanoparticles affected the flexural properties negatively. This result is consistent with those of Tian et al[18] who investigated composites modified with nanofibrilar silicates. This drop in mechanical properties is likely a result of the possible reinforcement due to higher nanoparticle loading being offset by particle entanglement and agglomeration, which were observed in the SEM analysis. Therefore, the second null hypothesis was also rejected. The spherical shape of nanoparticles should have advantages over irregular-shaped fillers regarding particle dispersion. Because spherical particles have only one point of contact, the tendency to agglomerate would be reduced, as a small surface area is available for particle/particle attraction, and less energy is needed to break these interactions; however, this effect probably occurs for fillers with particle size differing only in morphology, which is not the case here.

Large mass fractions of nanoparticles mixed into hybrid composites have been associated with impairment of the mechanical properties and formation of filler agglomerates in resin-based composites.[18] The presence of large clusters formed by small particles is also observed in commercial nanostructured restoratives.[13] The main point regarding the clusters is the connective status of the nanoparticles. Under stress loading, the connectivity between the fillers and of the fillers with the polymer matrix is critical,[19] as a good link may halt the crack propagation in the matrix surrounding the fillers.[20] The interparticle spaces are very small inside the clusters; provided that strong connective forces between the nanoparticles themselves and the nanoparticles with the resin are obtained, these areas may have a protective effect in the structure. Poor connective forces, on the other hand, may lead the clusters to act as spots of stress concentration within the luting agent, impairing its mechanical properties.

Whereas incorporation of large fractions of nanoparticles negatively affected flexural properties, it increased hardness values. It has been shown that hardness and flexural data may not correlate well for resin luting agents,[21] which might be explained by differences between bulk and surface properties. High nanoparticle loads quickly saturate the resin phase because nanoparticles have a higher surface area than microparticles. Therefore, the surface of the composites occupied by fillers instead of the softer polymer phase is increased, leading to an increase in hardness.[22-24] This is a positive effect of nanoparticle incorporation into resin luting agents, as higher hardness values could be associated with increased wear resistance of the resin-based materials.[25]

The film thickness also increased as the incorporation of nanoparticles was incrementally added. An exponential increase in viscosity is associated with an increase in filler load; for identical filler fractions, the viscosity of the composite increases as the filler size decreases.[26] Due to the small particle size, the specific surface area of nanoparticles increases dramatically; therefore, more monomers are necessary to wet the surface of the particles. Additionally, as the filler load is increased or the filler size is reduced, in addition to the resin/particle interaction, there is an increase in the particle/particle interaction, decreasing the flow capacity of the luting agent. This might have a critical influence on the resulting thickness of the luting agent layer in clinical situations. It is important to highlight, however, that all luting agent films were below the 50-μm limit for dental luting agents in the ISO 4049 specification.[27]

The present results show that the judicious incorporation of silanated silica nanoparticles may improve the properties of hybrid resin luting agents. Under loading, nanoparticles may have the ability to reorient in a stress dissipation mechanism to inhibit crack extension in semicrystalline and amorphous polymers.[11,28] For surface coating polymers, crack healing mechanisms have been described in which nanoparticles are attracted to the substrate, filling surface defects.[29] However, mass fractions above 2.5% should be avoided as a detrimental effect on the properties becomes evident. The present results also show the incorporation of nanoparticles leads to formation of clusters within the mixed luting agent. This is corroborated by Tian et al[18] who reported that it was still a challenge to achieve a high degree of separation and uniform dispersion of silanized nanofibrilar silicates in a Bis-GMA/TEGDMA co-monomer. Differences in the protocol used to silanate the nanoparticles, however, may have an impact on both filler agglomeration and the connectivity status between the fillers and, therefore, affect the properties of hybrid resin luting agents.

Conclusion

Modest incorporation of nanoparticles may improve the properties of resin luting materials; however, nanofiller mass fractions above 2.5% should be avoided because they may be detrimental to the properties of the resin luting agents.

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