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MECHANICAL PROPERTIES OF DENTAL FILLINGS WITH NANOPARTICLES

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Abstract. Nanoparticles represent an innovative direction in dentistry that offers several possibilities for improving the physical-chemical properties of dental materials. Moreover, they may help to reduce tooth sensitivity and prevent the recurrence of tooth caries with their antibacterial properties. Particular attention is given to the significant potential of nanoparticles in enhancing the mechanical properties of dental fillings. Our aim was to use diamond nanoparticles to modify dental fillings based on glass ionomer cement (GIC) and evaluate the effects of nanoparticles on the hardness, strength, wear resistance, and surface texture of the composite. Results suggest that modification of GIC using diamond nanoparticles can be an effective method for improving mechanical properties and may lead to the development of improved materials for dentistry.

Keywords: Dental fillings, diamond nanoparticles, glass ionomer cement, mechanical properties, tribological properties.

1. Introduction

The safety of amalgam fillings has been a contentious issue in dentistry. Concerns have primarily centred on the risks associated with the handling and use of amalgam materials, including potential exposure to mercury vapours by healthcare professionals, allergic reactions to the metals contained in amalgam, and the challenges related to the safe disposal of amalgam waste. In response to these risks, alternative dental filling materials have been developed and studied, with an emphasis on their safety and ability to replace amalgam fillings [1, 2].

In the latter half of the 20$^{\text{th}}$ century, initial mentions of alternative dental filling materials emerged; one is, for example, Glass Ionomer Cement (GIC). Since its introduction, GIC has undergone significant advancements and numerous innovations, establishing itself as a self-curing material predominantly used in restorative dentistry. It is particularly effective for treating deciduous teeth, Class III and V caries, and minor Class I and II caries [3, 4]. GIC exhibits reduced moisture sensitivity at the dental filling application site compared to photocomposites. The moist environment within the oral cavity is beneficial for GIC, as water acts as a reaction medium in the initial stages and facilitates the gradual hydration of the crosslinked chains in the subsequent stages [5, 6].

GIC offers several notable benefits, including the release of fluoride ions, strong adhesion to dentin and enamel, promotion of partial remineralisation of dental tissue, and excellent biocompatibility. However, despite these advantages, GICs are currently limited by their inadequate mechanical properties, which constrain their broader use and impact their durability in clinical settings [7]. The mechanical strength of dental fillings is critical, as it determines the material's ability to withstand the compressive forces generated during mastication. Hardness, on the other hand, reflects the material's resistance to wear and abrasion, which is crucial for the longevity of dental restorations [8]. One additional factor that affects the resulting characteristics of GICs is surface roughness. This has a substantial impact on the adhesion between the filling and the dental tissue and influences interactions with microorganisms and salivary components present in the oral cavity [9, 10].

The incorporation of nanoparticles into dental fillings presents a promising way for advancements in dentistry. Nanoparticles offer the potential to enhance the mechanical properties, wear resistance, and antibacterial activity of fillings, thereby extending their lifespan and contributing to improved patient outcomes. However, identifying suitable nanoparticles for this purpose requires considerable research and development efforts [11].

This research evaluates the change in performance of a commercially available glass ionomer cement (GIC) modified with nanoparticles (dimensions less than

100 nm). The dimensions, morphology, chemistry, or surface modification of these nanoparticles significantly influence the physicochemical characteristics of the composite material in which they are used. This research aims to assess the mechanical, physical, and tribological properties of the newly developed composite materials suitable for dental purposes. The findings are compared with commercially available GICs commonly employed in clinical practice.

2. Materials and methods

2.1. Glass ionomer cement

Glass Ionomer Cement (GIC) is a dental filling material composed of a powder and a liquid. The powder consists of finely ground silica glass, calcium, aluminium, and fluoride compounds. The liquid is polyacrylic acid. When these two components are mixed in precise proportions, an acid-base reaction occurs, forming a solid material upon solidification [5, 6]. SDI Riva Self Cure glass ionomer cement (GIC), manufactured by SDI Dental Limited, as a powder/liquid system was used in our research. The powder and liquid components are mixed in a 1:1 ratio, corresponding to one drop of liquid and one plastic scoop of the powder component. The measuring plastic scoop is part of the package. The mixing time of both components should be approximately 30 seconds, while the solidification time of the GIC is around 2 minutes.

2.2. Nanoparticles

Nanoparticles of diamond (ND, Adámas Nanotechnologies, 30 nm) and modified ND (ND-OH, hydroxylated detonation nanodiamonds, Adámas Nanotechnologies, 30 nm) were used. Nanoparticles were selected for their mechanical properties and biocompatibility. The added nanoparticles to the GIC were at 0.25 wt% and 0.50 wt% concentrations (the concentration was calculated for the powdered component). The nanoparticles were integrated into the powder phase of the GIC using a mortar and pestle. The resulting mixture was homogenised by mechanical stirring in a digester for several minutes. This procedure was established based on a pre-determined methodological framework. The sample without adding nanoparticles, i.e., according to the manufacturer's instructions, was a control sample (reference samples). The research was focused on evaluating the effect of nanoparticles on the resulting utility properties of the composite and choosing the appropriate type of nanoparticles. The distribution of nanoparticles in the volume of the composite material and the amount and size of the resulting agglomerates will be the subject of further research. The following tables and graphs will identify the different sample groups by letters; see Table 1.

Sample	Nanoparticles [wt%]
A	Reference sample (no modification)
B	ND 0.25 %
C	ND 0.50 %
D	ND-OH 0.25 %
E	ND-OH 0.50 %

Table 1. Designation of sample types.

2.3. Sample and experimental set-up

The GIC powder and nanoparticles were thoroughly mixed and enclosed in well-sealed containers. The samples were prepared per the instructions for the commercially used GIC, i.e., the powder portion was put on a glass slide using a plastic spoon, and the liquid portion of the GIC was measured using a dropper (part of the package). The amount of powder (or powder with nanoparticles) and liquid depended on the size and shape of the sample required; a ratio of 1:1 was always maintained:

a) Cuboid shape with dimensions $25 \times 4 \times 4$ mm (length × width × height), according to ISO 4049:2019 Dentistry – Polymer-based restorative materials. Due to the 3-point bending tests, the size of the samples had to be adjusted (by doubling the height and width of the samples).

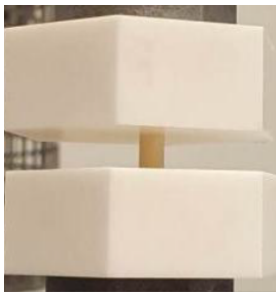
b) Cylinder shape with dimensions ∅ 4 mm, height 6 mm, according to ISO 7489:1986 Dental glass polyalkenoate cements.

The specific-shaped silicon mould was used to create cuboidal or cylindrical samples (see above; only the lateral sides of the composite came into contact with the mould; a glass square applied pressure to the top and bottom sides of the sample placed at the same time in the mould for a maximum of 3 minutes). Once the composite had dried, the sample was easily removed from the mould. Without any additional surface treatment, the samples were stored in an Eppendorf tube with a few drops of distilled water (as a crack prevention) at room temperature.

2.4. Mechanical-physical properties

The **compressive strength test** (Figure 1a) was carried out on 5 cylindrical specimens (see Section 2.3b) using a Testometric machine based on ISO 4506. The machine jaw feed speed was 0.05 mm min^{-1}, the preload was 300 N (to shorten the test, the preload that the sample should withstand is set to avoid starting from 0 N), and the force drop was 50 % Fmax. Upon reaching the maximum load capacity, the material's structural integrity begins to degrade. The test is concluded when the load capacity diminishes to 50 % of the maximum recorded load. Specimen failure ended the compressive strength test.

The **3-point bending test** was performed on the 5 cuboid specimens (see Section 2.3a) using the 3-point bending method at Bruker Nano Surfaces Division (Figure 1b). The feed rate of the machine's top roller was approximately 0.02 mm s^{-1}, and the initial position of the top roller was approximately 13 mm above



(A). Compressive strength test.

(B). 3-point bending test.

FIGURE 1. Conducting experimental activity.

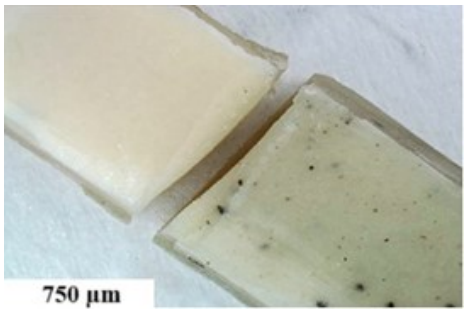


FIGURE 2. Samples of glass ionomer cement without and with nanoparticles of nanodiamonds (sample B).

the test specimen. The distance between the lower support rollers was 20 mm, and the diameter of one roller was 5 mm. The same method was used for adhesion tests between the materials (the modified GIC to the reference GIC).

For **hardness measurements**, the device used Struers Duramin-40 on block samples; with the Vickers method, a load of 0.015 kg and ten indentations were performed on each tested specimen with 1 mm spacing between each indentation. The surface roughness of the samples is described in Section 3.4, which provides the average Sa values for all samples.

The **tribological test** was performed using the Anton Paar TRB^3 tribometer (which complies with ASTM G99 and ASTM G133 standards) with the linear reversible method. 5 cuboid specimens (see Section 2.3a) and a ceramic sphere (Al_2O_3) with a diameter of 6 mm as the test counter-body were used; the load was set at 5 N, and the ball's movement speed on the composite's surface was at 4.50 cm s^{-1}; the total travel distance was 10 m. At the end of the test, using a SENSOFAR S Neox confocal microscope, the wear based on the width and depth of the wear track was evaluated. As part of the research, the experimental work was aimed at evaluating the amount of wear of composite materials before and after modification with nanoparticles. The aim of the experiment is not to simulate chewing processes in the oral cavity, but the resistance of modified composite materials to the action of external forces during the preservation of moisture of the composite material.

2.5. Confocal microscopy

The samples' surface roughness was examined using a SENSOFAR S Neox confocal microscope at 20x magnification. The samples were prepared in special silicone moulds that ensured the necessary surface quality. The sample preparation is described in Section 2.3, while the surface structure is defined using a silicone mould or a glass square. Therefore, there was no need to perform additional treatment of the surface of the samples as part of further measurements. Measurements were taken at five locations in the centre of the block sample. According to ISO 25178, the height parameter (Sa, arithmetical mean height of the surface) was evaluated, including the statistical distribution of height values along the z-axis. Material surface characterisations were processed using Gwyddion (a modular program for visualising and analysing height field data, accessible and open-source software).

2.6. Statistical analysis

The results for the mechanical properties are tabulated as median and first and third quartiles (Q1 and Q3), as they provide the most reliable performance when comparing distributions between groups. They were chosen because these tests had more outliers, which skewed the average. The tribological properties and adhesion results are shown as bar graphs of means with a standard deviation (a better expression for the data where standard distribution may be assumed). A one-way ANOVA test for statistical analysis was used.

3. Results and discussion

3.1. Analysis of mechanical-physical properties

We took measurements seven days after sample preparation (example in Figure 2). During the first few days, the GIC is still "working" (so-called cement maturation); specific reactions occur through which the material matures, and its physical and mechanical properties are constantly improved. After seven days, the material is sufficiently mature and its properties change minimally thereafter.

For the reference specimens (Group A), compressive strength was measured at 100.1 MPa after seven days, and flexural strength was 42.3 MPa (Table 2). The compressive strength was comparable to the reference specimens for the modified specimens Group B and C (both ND), and Group D (ND-OH 0.25 %) was evaluated with a 12 % reduction in values. A slight value increase (of about 14 %) was observed only for the samples with higher modified nanodiamond content, 114.9 MPa Group E (ND-OH 0.50 %). The flexural strength decreased for all samples with nanoparticles; only the samples in Group E (ND-OH 0.50 %) achieved values similar to the reference samples, reaching 40.7 MPa (lower by about 4 % than Group A). Nanoparticles can affect GIC flexural strength and

Group	Compressive strength [MPa]			Flexural strength [MPa]			Vickers microhardness test [$HV_{0,015}$]		
	Median	Q1	Q3	Median	Q1	Q3	Median	Q1	Q3
A	100.1	89.6	112.8	42.3	40.9	53.4	57.9	54.5	60.0
B	97.7	80.6	101.4	27.6	22.2	34.1	37.6	31.4	40.4
C	95.4	82.3	103.7	19.0	17.1	19.4	47.0	37.6	64.0
D	88.7	64.1	108.6	27.8	22.0	37.1	40.9	36.6	46.7
E	114.9	104.8	115.4	40.7	28.7	52.2	35.1	34.4	38.7

Table 2. Results of mechanical properties of the samples (designation according to Table 1).

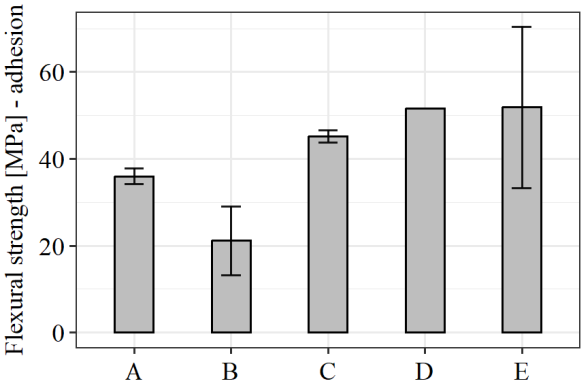
compressive strength. However, compared to composite resin dental fillings, both parameters measured for modified GICs (Group E) are twice as low [12, 13].

In the case of microhardness, the added nanoparticles reduce the hardness of the material (Table 2). Although the samples with higher concentrations of ND nanoparticles showed higher values (47.0 $HV_{0.015}$, Group C) than the other samples, they did not exceed the values of the reference samples (57.9 $HV_{0.015}$, Group A).

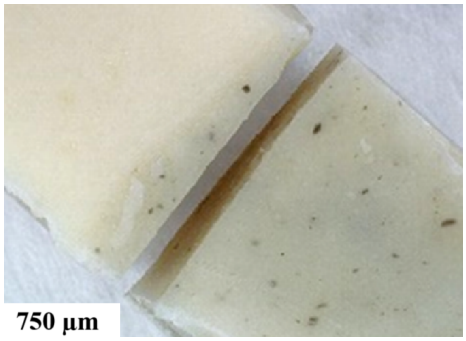
3.2. Adhesion of composite materials

Adhesion of the dental material refers to its ability to adhere effectively to the tooth surface, which is necessary to maintain the stability of the filling and prevent the penetration of bacteria or fluids between the filling and the tissue. The process of preparing adhesion tests is known to be a complex and multifaceted endeavour, involving a range of factors that must be taken into account (e.g., permission to test on a human specimen, tooth preparation for the dental filling, instrument set-up); therefore, we chose an alternative method to assess the adhesion of modified GIC specimens to the GIC reference material. First, we created a half-block size sample (Section 2.3a) from a GIC without modification (Group A, reference material has been filled to half the length of the mould). After about 2 minutes, when the material had sufficiently solidified but not completely hardened, the second half of the mould was filled with modified GIC (ND, ND-OH) or with the reference GIC. After seven days of solidification (stored in an Eppendorf tube with a few drops of distilled water), samples were tested by the 3-point bend method.

The highest adhesion value was reached for the samples with higher ND content (Group C) and in both ND-OH concentrations (Group D and E). In contrast, we observed (Figure 3) poorer results for the samples with ND at lower concentrations (Group B). It is important to note that the results from the adhesion tests are only indicative and should be considered along with other relevant information. For example, in practice, the tooth is pretreated before the filling is applied and the surface roughness of the tooth (tissue matter) and the material surface changes. A significant advantage of GIC is that there is no need for an ideally dry surface for adhesion of the filling to the tooth, as is the case with photo composites, for example.



(a). A bar graph of mean values with standard deviations of the flexural strength of the modified GIC to the reference GIC.



(b). Broken sample C (left side unmodified GIC, right side modified GIC).

Figure 3. An adhesion test.

3.3. Wear resistance

Various factors can cause the wear rate of dental fillings. Abrasion of dental fillings can lead to gradual erosion or flaking and may require repair or replacement.

Figure 4a shows that the samples containing ND with lower and higher concentrations (Group B and C) had lower wear depth compared to the reference samples (Group A); the sample with higher concentrations (Group C) also had a smaller wear width (Figure 4b). Research has shown that the presence of nanodiamonds may reduce the wear of the GIC composites. For some samples, more sample fragments

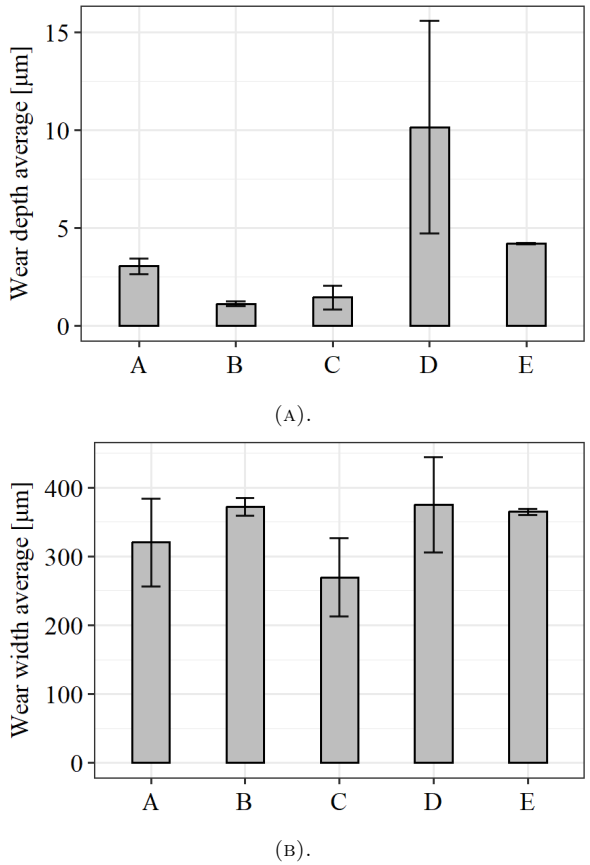


FIGURE 4. Wear test. A bar graph of mean values with standard deviations for (a) the wear track depth and (b) the wear track width.

(quantity or volume) were removed during the tests, as indicated by the higher standard deviations. The results in Figure 4 are too limited to conclude that the addition of a small amount of diamond powder improves wear resistance. More detailed observations are necessary.

3.4. Composite surface roughness analysis

The surface roughness parameter Sa was evaluated (Figure 5) and the results were processed according to the ANOVA statistical method. The height parameters (Table 3) show that the average surface roughness measured for the reference sample was 220 nm. Lowest surface roughness was measured for the samples with ND modification at higher concentrations (Group C, lower by about 27 % than group A) and with ND-OH modification at lower concentrations (Group D, lower by about 14 %). The highest surface roughness was measured for samples with ND modification at lower concentrations (group B, higher by about 39 %) and with ND-OH modification at higher concentrations (group E, higher by about 22 %).

3.5. Discussion

This study (Figure 5, composite samples) explored the impact of nanodiamonds (NDs) and hydroxylated

	Sa, arithmetical mean height of the surface [nm]		
Group	**Median**	**Q1**	**Q3**
A	220.2	215.5	242.2
B	306.5	275.5	379.2
C	173.2	154.3	283.1
D	193.5	182.5	201.1
E	269.1	235.0	313.2

TABLE 3. Height parameters of samples as a result of confocal microscopy.

nanodiamonds (ND-OH) on the mechanical and tribological properties of glass ionomer cements (GICs). The incorporation of higher concentrations of ND-OH increased compressive strength and flexural strength, reaching values of 114.9 MPa and 40.7 MPa, respectively. While ND and modified ND particles influenced the mechanical and tribological properties of GICs, the significance level of 5 % was not exceeded in any of the measurements. The results from other studies on materials commonly used for dental fillings showed that commercially available dental composites exhibit maximum compressive strengths of approximately 210 ± 1.8 MPa and flexural strengths of 119.6 ± 2.3 MPa. In comparison, amalgam displays compressive strengths of 199.5 ± 1.8 MPa and flexural strengths of 17.7 ± 1.1 MPa [12, 13].

Despite the slight improvement in compressive and flexural strength in the modified GIC samples (of about 15 %), these values remained close to those of the reference samples, indicating that the modifications did not substantially enhance the mechanical properties of GICs. The modified GICs in our study do not reach the values of other restorative materials. Furthermore, all modifications in this study led to a decrease in microhardness relative to the reference samples (commercially available GICs), which is consistent with findings in other research [14]. This decrease in microhardness may be attributed to several factors, such as nanoparticle aggregation, insufficient nanoparticle distribution (short processing time of the composite), disruption of the GIC matrix, incompatibility of nanoparticles with GIC components (low particle adhesion to the matrix), or alterations in chemical reactions (inclusion of a non-native component in the GIC).

The incorporation of ND at both concentrations resulted in up to a 50 % reduction in the wear depth of GICs compared to the reference samples, which proved significant at a level of 5 %.

For future research, it would be advantageous to simulate the oral environment, particularly with respect to humidity levels, as material drying was observed during measurements. In addition, conducting dynamic tests that partially mimic masticatory processes would provide more pertinent insights. It is crucial to acknowledge that all results remain indica-

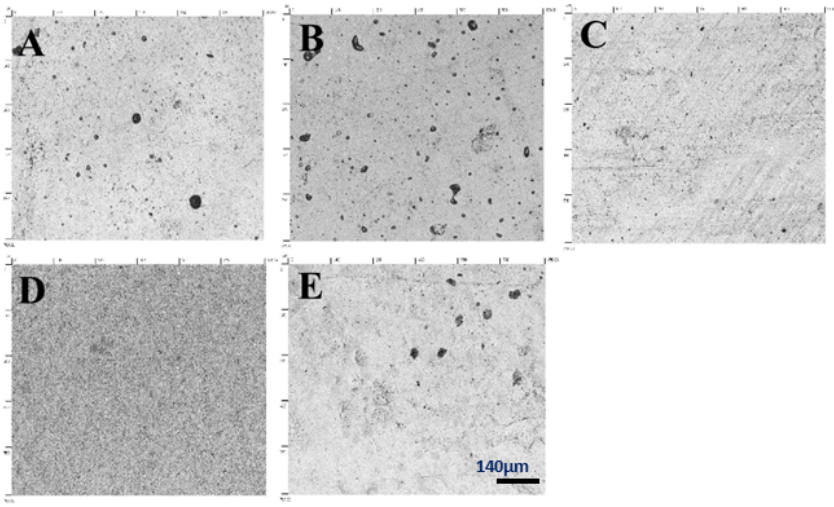


Figure 5. Images of sample surface with 20x magnification (confocal microscopy). The scale is the same for all images: 140 µm.

tive, as a complete simulation of the oral environment is inherently challenging. Variability in bite force, biting frequency, force composition, and genetic and ethnic predispositions all contribute to the longevity of dental restorations, making it difficult to standardise testing conditions that accurately reflect individual patient experiences.

4. Conclusions

In this research, two types of diamond nanoparticles were used in two different concentrations, which were added to the base GIG composite material. The change in mechanical and tribological properties after the modification of the composite with diamond nanoparticles was mainly monitored. A slight improvement in compressive strength was observed, while the flexural strength and microhardness were significantly lower than the reference GIC for all tested modifications (up to 55 % and 39 %, respectively). Adhesion tests revealed that nanoparticles can enhance the composite's adhesive strength. However, the wear depth was up to half lower for pure nanodiamonds (ND) and up to three times higher on average for ND-OH, indicating that the chemical modification of nanoparticles plays a crucial role within composites. It has been clearly demonstrated that the addition of diamond nanoparticles leads to a significant reduction in the amount of wear of the composite. The application of nanotechnology in dentistry offers significant potential for improving and advancing dental materials; however, a detailed study is still necessary.

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