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TiO_2 nanotubes improve physico-mechanical properties of glass ionomer cement

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ABSTRACT

Objectives. The aim of this study was to determine the physico-mechanical properties of a high viscosity glass ionomer cement (GIC) reinforced with TiO_2 nanotubes (TiO_2-nt).
Methods. TiO_2-nt was incorporated into the GIC powder components (Ketac Molar EasyMix™) in concentrations of 0% (control group), 3%, 5%, 7% by weight. Compressive strength (n = 10/group), three point bending for flexural strength (n = 18/group), microshear bond strength

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to dentin and failure mode (n = 20/group), and surface roughness and weight loss before and after brushing simulation (30,000 cycles) (n = 8/group) were evaluated. Data were submitted to Shapiro-Wilk, ANOVA, Tukey and Chi-square tests ($\alpha \leq 0.05$).

Results. Addition of 5% of TiO_2-nt into GIC presented the highest values for compressive strength and differed from the control, 3% and 7% groups ($p = 0.023$). There were no significant differences in flexural strength ($p = 0.107$) and surface roughness before and after the dental brushing ($p = 0.287$) among the groups. GIC added with 5% TiO_2-nt showed the lowest weight loss values ($p = 0.01$), whereas the control, 3% or 5% TiO_2-nt groups presented similar microshear bond strength values ($p \geq 0.05$). The 5% TiO_2-nt group featured higher microshear bond strength than the 7% TiO_2-nt group ($p = 0.034$). Cohesive in material was the most representative failure mode for all groups.

Significance. The incorporation of TiO_2-nt did not affect GIC's adhesiveness to dentin, but improved its compressive strength at 5%. Furthermore, TiO_2-nt decreased the percentage of weight loss after GIC's surface wear.

1. Introduction

Glass ionomer cements (GIC) were first introduced into the market at the end of the 70 s, and since then their composition has been modified to become more appropriate for different clinical situations [1]. The powder of conventional GIC is mainly composed by silica (SiO), alumina (Al_2O_3) and calcium fluoride (CaF_2), with an alkaline composition, while the liquid contains polycarboxilic acid as a co-polymer with itaconic acid, tricarboxylic, maleic or tartaric, which increases the strength of the set cement and decrease its viscosity [1,2]. When mixing the powder and the liquid, the set reaction begins to form a hydrated salt, which acts as a bonding matrix for the glass particles [1,3]. Among the reported GIC properties, adhesion to dental structure, linear expansion coefficient similar to that of the tooth, biocompatibility and anticariogenic action due to the release of fluoride are highlighted [1,4,5]. On the other hand, GIC has been reported to feature limitations, including high initial syneresis and imbibition that can result in dimensional changes, decrease of surface wear resistance and the formation of cracks and gaps [6]. Such limitations may contribute to restoration failure with the possibility of bacterial proliferation and secondary caries lesions and/or restoration fractures, especially restorations performed as atraumatic restorative treatment (ART) in areas of great masticatory effort and involving multiple surfaces [7,8].

In order to overcome the above-mentioned limitations, the incorporation of different nanoparticles to GIC has been proposed, including metallic powders, montmorillonite clay, cellulose, zinc, silica, ceramics, ytterbium fluoride and barium sulfate, hydroxyapatite and fluoroapatite, aluminosilicate glass, casein phosphopeptide-amorphous calcium phosphate, bioactive glass and titanium dioxide [9,10,12–20]. In general, it has been found that not all modifications have resulted in the desirable strengthening of GICs. For instance, metallic oxides and salts such as SrO and $BaSO_4$ did not affect GICs' mechanical properties as they lacked the ability to increase the number of polysalt bridges and cross-linking within the glass matrix [10]. Moreover, although bioactive glass alone led to an increased bioactivity, it decreased the material's strength [10,19].

Titanium stands out because it is an inorganic additive, chemically stable, non-toxic and may present antimicrobial effects [11]. Although some progress has been made with respect to the benefits of adding TiO_2 nanostructures to conventional GICs [10,12–14,16,18], there is a lack of evidence on the specific impact of TiO_2-nt on the physico-mechanical properties of GICs. Main limitation of previous studies included the fact that they used spherical-shaped nanostructures, which tended to form clusters rather than permeate the GIC's matrix [9,12–14,18]. Tubular materials, such as TiO_2-nt, are hollow nanostructures that feature a high surface-to-volume ratio [21], which may contribute to improved surface energy, as well as better particle distribution, improving GIC's overall properties. In a previous study, it has been demonstrated that GICs added with TiO_2-nt presented improved surface microhardness and fluoride release at concentrations of 3% and 5%, while EDS analysis detected the presence of TiO_2-nt into the material at 5% and 7% [16]. However, additional studies are needed to determine the effect of TiO_2 at nano-tubular shape on GIC's adhesion properties to dentin, compressive and flexural strength; providing the basis to establish restoration longevity [18,22,23], as well as for the use of GICs in areas of high masticatory loads.

Therefore, the aim of this present study was to analyze the impact of the incorporation of the TiO_2-nt to the conventional GIC on its physico-mechanical properties. The hypothesis of the current *in vitro* study were that the incorporation of TiO_2-nt to the conventional high viscosity GIC would affect its: (a) compressive strength; (b) flexural strength; (c) microshear bond strength to dentin; (d) failure mode to dentin; (e) surface roughness before and after brushing simulation; and (f) weight loss before and after brushing simulation.

2. Materials and methods

2.1. Grouping of specimens

The factor under study was the incorporation of different concentrations of TiO_2-nt (3%, 5% and 7% by weight) into a high viscosity GIC (Ketac Molar EasyMix™- 3 M/ESPE, Maplewood, Minnesota, USA). Four different experimental groups were obtained: Ketac Molar (KM) = control; KM + 3% TiO_2-nt; KM + 5% TiO_2-nt and KM + 7% TiO_2-nt. Evaluated parameters included: compressive strength (n = 10/group); flexural strength (n = 18/group); microshear bond strength to dentin and failure mode (n = 20/group); roughness surface and weight loss before and after brushing simulation (n = 8/group). This study was conducted after approval of the research ethics committee (CAAE #64,262,617.3.0000.5374).

2.2. Specimens preparation

TiO_2-nt at three different concentrations (3%, 5% and 7% in weight) were added to the powder of the GIC [aluminum-calcium fluorosilicate-lanthanum glass, 5% polycarbonate acid; shade A3], and then mixed to the liquid [polycarboxilic acid and tartaric acid] (Batch # 635,287; 638,396). Nanotubes (size ~20 nm and diameter ~10 nm), were formed by a single TiO_2 leaf spirally rolled and synthesized by the alkaline method [24]. A precision scale accurate to 0.0001 g (Adventurer Oshaus, Parsippany, NJ, USA) was used to determine KM's powder and TiO_2-nt weights. After weighing the materials, nanotubes were manually added to the GIC powder at different concentrations (3%, 5%, 7% by weight) as previously proposed [16]. Material agglutination was performed following the manufacturer's instructions for powder/liquid ratio (1:1) using a metallic spatula and a block of waterproof paper. Specimens were prepared at room temperature (23 ± 1 °C and 50 ± 5% relative humidity in accordance with ISO 7489) following the recommendation by the manufacturer. In brief, GIC with or without TiO_2-nt was placed in bipartite molds, inserted in a single increment with help from a Centrix syringe (Centrix Inc., Shelton, Connecticut, USA), and pressed between polyester strips (Proben, Catanduva, SP, Brazil) under a glass slide with a static load of approximately 200 g for 6 min. Next, specimens were covered with a thin layer of petroleum jelly (Rioquímica, São José do Rio Preto, SP, Brazil, batch#1,702,146) and stored for 24 h at 37 °C in relative humidity. After 24 h, the excess of petroleum jelly was gently removed with a soft paper from the specimen before conducting the tests [16].

2.3. Compressive strength (CS)

Cylindrical specimens (6 × 4 mm) were prepared (n = 10/group, ISO 9917-1) and analyzed as previously described (ISO 9917-1) [25]. CS was calculated (MPa) using the equation $C_S = \frac{4P_f}{\pi D^2}$, where Pf represented the fracture load (Newtons), and D represented the diameter of the specimen (mm).

2.4. Flexural strength (FS)

Specimens (25 × 2 × 2 mm) were prepared (n = 18/group) and the FS test was performed based on the ISO 9917-2 [25], subjected to three bending points on a 20 mm device in a universal testing machine. FS was determined (MPa) using the formula $\sigma = \frac{3Pl}{2bd^2}$, where P (Newtons) represented the breaking load, L the distance between the two supports of 10 mm, b the sample width (mm) and d represented thickness (mm).

2.5. Microshear bond strength to dentin substrate (MSBS)

Human third molars (n = 20/group), extracted for orthodontic reasons and free from apparent caries, macroscopic cracks, abrasions and staining on the occlusal surface were selected (assessed by visual examination of radiographs with the assistance of magnifying lenses). Teeth were cleaned and frozen until processing time. Their roots were sectioned off 1 mm beyond the cement-enamel junction using a double-faced diamond saw (KG Sörensen, São Paulo, SP, Brazil). Crowns were longitudinally sectioned by a water-cooled diamond blade (Isomet 1000, Buehler Ltda., Lake Bluff, IL, USA), and each half was included in rigid PVC rings (Tigre, Joinville, SC, Brazil) with self-curing acrylic resin (JET-Classic, São Paulo, SP, Brazil). The inner surfaces were planned with 340 grit sandpaper (Buehler, Lake Bluff, IL, USA), polished with 600 grit sandpaper (Buehler) (ISO 6344-1:2014) [26], rinsed with water spray, gently dried, and randomly assigned to one of the experimental groups. Next, dentin was actively conditioned with polyacrylic acid for 10 s, air-dried, and three siliconized polyvinyl cylinders (2 × 0.8 mm) were filled with the control and experimental materials on the medium dentin surface. MSBS values were obtained following the formula $\tau = \frac{F}{A}$, where F represented the force obtained during the test (Newtons), and A represented the area subjected to the micro-shear test (mm^2). The average value of the three cylinders for each group was used for statistical analysis [27,28].

2.6. Failure mode analyses

Failure mode produced after the MSBS tests was defined under a stereoscope (40× magnification, Eikonal EK3ST, São Paulo, SP, Brazil) and validated by SEM analysis (100× magnification, 15 kV, WD = 16 mm, spotsize = 25) (n = 20/group) as cohesive in dentin, cohesive in material or mixed. Failure modes were determined twice in a one-week interval by a calibrated examiner (Spearman correlation test with 95% intra-examiner coincidence).

2.7. Surface roughness and weight loss

Specimens were prepared (n = 8/group), polished with medium, fine and ultrafine aluminum oxide polishing discs (15 s/disc) (Sof-Lex Pop On, 3 M Dental Products, MN, USA), cleaned by ultrasound for 10 min (T1440D, Odontobrás, Ribeirão Preto, SP, Brazil), and submitted to brushing abrasion in an abrasion-testing machine (Biopdi, São Carlos, SP, Brazil) as previously reported [29,30,36]. Briefly, thirty thousand cycles were performed at the speed of 250 strokes/min

(complete forward and reverse movements), with a load of 200 g, with soft bristles tips (Palmolive, São Bernardo do Campo, SP, Brazil), corresponding to three years of brushing. Baseline and final data were collected in triplicate prior and after tooth brushing abrasion simulation. In the current study, CS, FS, MSBS tests were performed in a universal testing machine at a crosshead speed of 1 mm/min, and a load of 50 N (EMIC DL200, Campinas, SP, Brazil).

2.8. *Surface characterization by scanning electron microscopy (SEM)*

In order to determine the impact of TiO_2-nt on the GIC's structure, samples were submitted to SEM analysis (JEOL- JSM 5600 L V, Tokyo, Japan) (n = 3/group). Briefly, GIC samples were prepared as described above, with or without TiO_2-nt, left to dry for 24 h, sputtered with a thin gold layer (Sputter Coater S150A, Japan), and analyzed at 1000× magnification in a working distance of 10 mm at 15 kV [13,16].

2.9. *Statistical analysis*

Data were analyzed using the Shapiro-Wilk normality test and Levene's homoscedasticity ($p \leq 0.05$). Analysis of variance (ANOVA) followed by the Tukey test was used to compare more than two groups, whereas the Dunnett's test was used to access statistical differences between the control group (without TiO_2-nt treatment) and TiO_2-nt groups at different concentrations. The relative frequency (in %) followed by the chi-square test was used for failure mode. Analyzes were performed using a software (SPSS 21, Chicago, IL, USA), and the level of significance was 5% ($\alpha \leq 0.05$).

3. Results

Data analysis showed that the 5% TiO_2-nt group presented the highest CS mean values as compared to the other experimental groups (p = 0.023), whereas the one-way ANOVA test demonstrated that there were no significant differences among the groups regarding FS (p = 0.107) (Table 1). In addition, intergroup analysis revealed that the 5%TiO_2-nt group featured higher MSBS values than the 7% TiO_2-nt one (p = 0.034), and presented non-significant differences as compared to the 3% TiO_2-nt and KM (control) groups. In the present study, intergroup analysis further revealed an overall prevalence rate of 12.92% of premature failures, defined as failures occurring before the failure mode analyses were performed. Cohesive in material was the only failure mode found accross the experimental groups, with no significant differences among the experimental groups (p = 0.678). Fig. 1 illustrates the pattern of failure mode for the experimental groups. Intra and intergroup analysis did not detect significant differences for surface roughness (p = 0.287 p = 0.106, respectively), whereas intergroup analysis showed that TiO_2-nt significantly decreased GIC's matrix weight loss regardless of its concentration (p = 0.001) (Table 2). The lowest percentage of weight loss was observed for the 5% TiO_2-nt group. As far as a potential impact of TiO_2-nt on GIC's structure, data analysis demonstrated that the addition of TiO_2-nt to GIC did not resulted in relevant changes. Fig. 2 illustrates representative findings for SEM characterization of the impact of TiO_2-nt on GIC's structure.

4. Discussion

In the present study, all groups were found to reach the recommended minimum compressive strength values of 65 MPa [31]. However, the incorporation of 5% TiO_2-nt promoted a significant compressive strength improvement as compared to the remaining groups (p = 0.023), and we speculate that an improved GIC's matrix interaction acting as a reinforcement between the glass particles of the GIC powder, may have accounted for these findings. Importantly, the presence of TiO_2-nt into the GIC has been confirmed by EDS analysis [16]. Similarly to previous studies [13,16,32], in the current work, GIC incorporated with 3% or 7% of TiO_2-nt revealed respectively excessive and insufficient amount of polyacrylic acid to interact with the glass powder. Therefore, these findings suggest that TiO_2-nt concentration is a critical aspect controlling GIC's resistance outcomes, and are in agreement with previous reports on TiO_2-nt with similar size (20 nm) and a different format (spherical) [10,13–15,18,31].

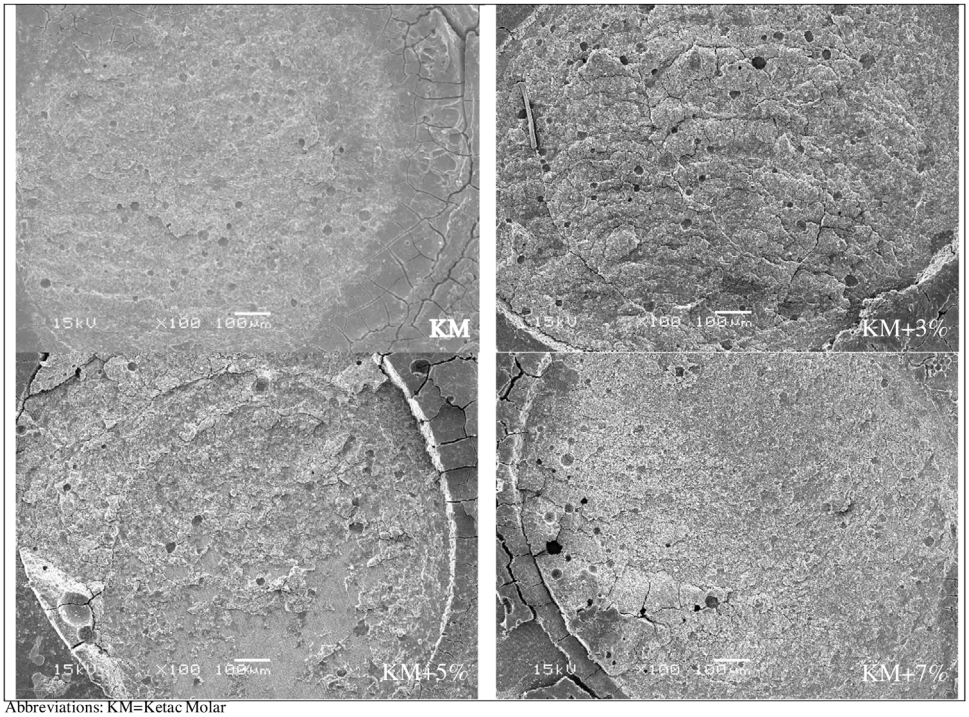
In the present investigation a trend towards an increased flexural strength was noted for the TiO_2-nt groups, demonstrating a potential impact of nanotechnology on GIC's resistance. Flexural strength has been reported to be affected by nanoparticles at 3% and 5% as compared to the GIC alone [13–15,17,18], with a strong correlation between flexural strength and amount of material's wear, *e.g.* the higher the material's resistance the lower its wear [32]. In the current study, the impact of TiO_2-nt on GIC's weight loss after 30,000 cycle abrasion test was assessed and data analysis showed that the 5% TiO_2-nt group featured the lowest abrasion levels (%), confirming an improvement in wear resistance in the presence of TiO_2-nt. It has been shown that the rate of weight loss depends on several factors including type of dentifrice, water/dentifrice ratio, type of brush, and speed and pressure employed during brushing [33]. In the current investigation, potential factors affecting material's weight loss were similar across the experimental groups, and therefore, abrasion resistance was found to depend on the concentration of TiO_2-nt. These findings are in agreement with previous studies on conventional or resin-modified GIC [34–36]. As previously suggested [16], in the current study we speculate that an increased surface hardness may have accounted for a lower weight loss rate in the 5% group. Moreover, addition of TiO_2-nt to GIC may have reduced the interparticle spacing, effectively protecting the softer matrix, reducing incidence of exfoliation, and increasing the overall abrasion resistance of the material [37].

In the present study, regardless of the concentration used, TiO_2-nt did not affect GIC's surface roughness, suggesting that the tubular format of TiO_2-nt allowed appropriate particle distribution. Likewise, Cibim et al. [16] have reported that the incorporation of TiO_2-nt did not influence surface roughness of GICs. It has been proposed that nanostructure dimension (between 1 to 100 nm) in combination with larger glass particles may lead to an appropriate matrix wrapping resulting

Table 1 – Means and standard deviations for the performed mechanical tests in MegaPascal (MPa) for the experimental groups.

Experimental Groups	Mechanical Tests		
	Compressive Strength (n = 10/group)	Flexural Strength (n = 18/group)	Microshear Bond Strength to Human Dentin (n = 20/group)
KM (Control)	89.46 (14.05) **B**	6.41 (1.33) **A**	4.76 (2.88) **AB**
KM+ 3% TIO_2-nt	93.13 (17.90) **B**	6.87 (1.72) **A**	5.11 (1.65) **AB**
KM+ 5% TIO_2-nt	105.23 (11.19) **A**	7.41(1.23) **A**	5.30 (2.20) **A**
KM+ 7% TIO_2-nt	90.00 (15.46) **B**	7.63(1.60) **A**	3.46 (1.46) **B**

Different capital letters, in column, differ by ANOVA and Dunnett. Compressive strength, p = 0.023; Flexural strength, p = 0.1636; Microshear bond strength, p = 0.034.
Abbreviations: KM = Ketac Molar; TiO_2-nt = Titanium dioxide nanotubes.



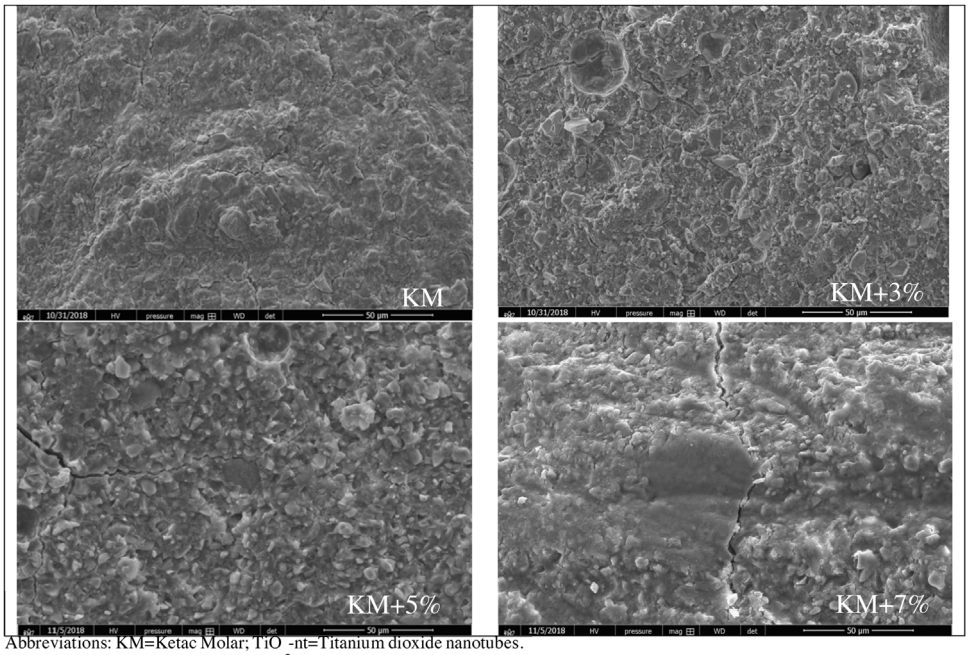
Abbreviations: KM=Ketac Molar

Fig. 1 – Representative SEM images illustrating the failure mode patterns. Note that for all the experimental groups the failure pattern was cohesive in material.
Abbreviations: KM = Ketac Molar.

Table 2 – Mean and Standard Deviation of the surface roughness values (μm) and the amount of weight loss (mg) at baseline and after tooth-brushing simulation in the experimental groups.

Experimental Groups (n = 8/group)	Surface Roughness		Weight Loss		Mass loss variation (%)
	Baseline (μm)	After (μm)	Baseline (mg)	After (mg)	
KM (Control)	0.3127 (0.24899) Aa	0.4213 (0.16156) Aa	0.0893 (0.01613)[a] Aa	0.0859 (0.01337)[a] Ab	3.8
KM+ 3% TIO_2-nt	0.4365 (0.09671) Aa	0.3916 (0.15252) Aa	0.1013 (0.01426) Aa	0.0980 (0.01412) Ab	3.3
KM+ 5% TIO_2-nt	0.3851 (0.17488) Aa	0.3997 (0.17892) Aa	0.0962 (0.01546) Aa	0.0948 (0.01511) Ab	1.4
KM+ 7% TIO_2-nt	0.3871 (0.12821) Aa	0.4133 (0.15179) Aa	0.1070 (0.01202)[a] Aa	0.1041 (0.01033)[a] Ab	2.7

Different upper case letters in columns demonstrate that there is significant difference among experimental groups for ANOVA Two-way repeated measures ($p < 0.05$).
Different lower case letters in rows demonstrate that there was significant statistical difference for surface roughness and weight loss, separately, when compared over time (baseline and after brushing) ($p < 0.05$).
Abbreviations: KM = Ketac Molar; TiO_2-nt = Titanium dioxide nanotubes.
[a] It shows there is significant difference between experimental groups for Dunnett.



Abbreviations: KM=Ketac Molar; TiO2-nt=Titanium dioxide nanotubes.

Fig. 2 – Representative SEM images (1000× magnification) illustrating the effect of TiO_2-nt incorporation (at 3%, 5% and 7%) on the structure of a conventional GIC (KM).
Abbreviations: KM = Ketac Molar; TiO_2-nt = Titanium dioxide nanotubes.

in a favorable surface roughness as compared to other dental materials in general [15,16,35]. In line with this hypothesis, in the current investigation SEM analysis showed that addition of TiO_2-nt did not alter GIC's structure as illustrated in Fig. 2.

It is well known now that the material's adhesiveness to the dental substrate, will play an important role on GIC's clinical performance [38]. In the current study, data analysis demonstrated that TiO_2-nt concentration directly impacted on the MSBS findings, with the 7% group featuring lower MSBS values than the other experimental groups (Table 1). These findings allow the conclusion that high concentrations of TiO_2-nt (≥7%) will lead to a deficient interaction between powder and polyacrylic acid, and negatively influence the chemical bond between GIC and the tooth. Similarly to the findings of the present study, Garcia-Contreras et al. [18] have reported that at lower concentrations (3% and 5%) TiO_2-nt did not interfere with GIC adhesion to the dental tissues. In contrast, El-Negoly et al. [14] reported that at 7% TiO_2 nanoparticles increased GIC adhesiveness. Material's adhesiveness has also been reported to be affected by the position of dentinal tubules and dentin depth [39–42]. Here, the observed fracture patterns further demonstrated that GIC's bond strength to dentin was higher than the values of cohesive strength, corroborating with previous studies [43–45].

Together, the findings of the present study suggest that the use of nanotechnology is a promising strategy to improve physico-mechanical characteristics of GIC. However, as the use of TiO_2-nt to improve GIC's clinical performance is a relatively new concept and the current investigation is limited to an *in vitro* experimental design that cannot fully mimic the "real" clinical setup, additional studies should be designed in order to further define the potential impact of TiO_2-nt on other GIC's properties, including syneresis and imbibition processes, material's aging on affected tooth, as well as longitudinal randomized clinical studies.

5. Conclusion

TiO_2-nt led to increased compressive strength without affecting GIC's adhesiveness to human dentin substrate and its structure. In addition, nanotechnology applied to GIC did not change its flexural strength or roughness, but decreased the percentage of weight loss after brushing simulation. Therefore, it can be concluded the use of TiO_2-nt to improve GIC's properties represents a promising strategy to improve its clinical outcome.

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