

# Synthesis of novel titania nanoparticles using corn silky hair fibres and their role in developing a smart restorative material in dentistry

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## ABSTRACT

**Objectives:** The oral healthcare sector is witnessing a significant increase in the creation of eco-friendly bio-materials intended to inflict minimal damage to humans and the environment, primarily due to the inadequacies of conventional synthetic restorative materials which have a short shelf life and are prone to instability. The main objective of this study was to synthesise cost-effective titania nanoparticles (TiO<sub>2</sub> NPs) from biowaste corn silky hair fibre.

**Methods:** The titania nanoparticles (TiO<sub>2</sub> NPs) were characterised through x-ray diffraction; scanning electron microscopy; energy-dispersive spectroscopy; Fourier transform spectroscopy, and atomic force microscopy, as well as dynamic light-scattering to identify their phases, morphologies, dimensions, and chemical compositions. The nanoparticles were subsequently integrated into standard glass ionomer cement (GIC) to create innovative smart titania-enriched glass ionomer cement at multiple concentrations in the form of 4 × 4 × 1 mm blocks, which were evaluated for enamel shear bond strength, spectral mapping, and surface topography.

**Results:** Confirmation was obtained that the newly synthesised TiO<sub>2</sub> nanoparticles, with a particle diameter of 24.17 nm and a pure rutile phase, displayed a spherical morphology and a smooth surface. Adding 5 % of these smart titania nanoparticles to GIC resulted in a substantial increase in its shear bond strength to enamel, which rose to 4.93 ± 0.74 MPa, with a standard error of 0.23, and this change was statistically significant at p < 0.05. The material's sustainable surface characteristics were confirmed by the presence of increased Fluorine (6.46 %) and Titanium (0.79 %) alongside a decrease in the amounts of Aluminium (23.51 %), Silicon (20.01 %), Phosphorus (0.33 %), and Sulphur (0.09 %), as indicated by spectral mapping.

**Conclusion:** This study developed eco-friendly and sustainable titanium dioxide nanoparticles from silky corn hair fibres. The addition of titania nanoparticles to conventional glass-ionomer cement resulted in increased enamel shear bond strength and altered surface texture with higher titanium and fluorine content, making it a promising smart restorative material for dentistry.

**Clinical significance:** A new smart material containing titania-enriched glass ionomer cement showed its ability to significantly improve enamel shear bond strength and extend its storage life. These eco-friendly biomaterials have considerable clinical potential to provide enhanced stability and performance in the oral environment.

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## 1. Introduction

The oral healthcare sector is increasingly acknowledging the necessity for eco-friendly restorative biomaterials that are safe for human use, the environment, and surrounding ecological systems. The creation of these materials poses considerable difficulties, primarily in reconciling the requirements of biocompatibility, durability, and environmental protection. Historically, synthetic restorative materials have been commonly employed to restore or substitute the human tooth structure but these materials frequently present potential hazards [1]. In clinical dentistry, the compatibility and sustainability of biomaterials are crucial, where they are affected by several factors, such as their synthesis protocols, chemical stability, surface features, composition, methods of use, physical properties, concentration, duration of exposure and the location in the oral cavity. In contrast, hazardous emissions from certain biomaterials take the form of fumes, dust particles, vapors, precipitates, liquids, and powders, potentially induce a detrimental effect on both human health and environmental security [2]. Therefore, there is a pressing need to develop biomaterials with the help of natural biowaste products that offer optimal sustainability and compatibility, ensuring safety for both patients and environment.

The fibre from Silky Corn hair, sourced from Corn silk (*Stigma maydis* L.), is a well-known natural waste product rich in various nutrient components, vitamins, and minerals, such as carbohydrates, proteins, vitamin K, vitamin A, vitamin B, potassium, and sodium. The compound contains multiple bioactive elements, including phenolic compounds, saponins, carotenoids, anthocyanins, alkaloids, and steroids, which have a substantial impact on health-related problems. The Corn Silk has been used in the treatment of common conditions including nocturnal enuresis, obesity, nephrolithiasis, and prostatic disorders. Additionally, it also serves to mitigate the hazardous effects of high blood pressure, hypertension, and diabetes. The anthocyanins found in Silky Corn hair fibre have demonstrated significant anti-inflammatory, anticancer, and antioxidant effects. The Silky Corn hair fibre (SCHF) has been proven as a candidate to prevent the formation of biofilm by certain bacteria in the oral cavity, which are known to cause dental caries, including *Streptococcus Mutans*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Bacillus subtilis* and others [3,4]. Therefore, Silky Corn hair fibre (SCHF) could serve as a pivotal, naturally accessible source for developing a clinically smart or active biomaterial.

Traditionally, inert biomaterials have been the preferred choice in clinical dentistry due to their perceived ability to prevent adverse reactions when interacting with oral fluids, dental structures, and surrounding soft and hard tissues, whereas active or smart materials were less commonly used. Despite their durability and stability, these materials frequently fell short of "high effectiveness standards" because they are unable to adapt to environmental changes; conventional glass ionomer cements (GIC) and resin modified GICs are examples, continuously releasing anticariogenic ions throughout their lifespan whether required or not, with the intention of preventing dental caries [5]. The unregulated flow of ions within the mouth may compromise the entire tooth's structure and any existing restoration ultimately resulting in problems such as wear, abrasion, tooth fracture, secondary caries, marginal leakage and restoration fracture later in life [6].

In comparison, active intelligent biomaterials have garnered greater interest due to their capacity to perceive and react to environmental stimuli in a regulated fashion. These materials are employed in a range of cutting-edge dental applications, such as restorations (smart GIC, smart Composites, smart prep burs), prosthodontics (smart ceramics, smart impression materials, orthodontics (shape memory alloys), paediatrics (APC releasing pit-fissure sealant, fluoride releasing sealant), endodontics (NiTi rotary instruments, smart biomaterials), and lasers (hollow core small photonic fibers), where the adaptive properties of these materials contribute to the improved clinical results [7]. These smart or active materials can alter their properties in response to fluctuations in pH, moisture, temperature, stress, magnetic and electric

fields, thereby making them more adaptable to the dynamic environment of the oral cavity. As a result, these materials have been classified as advanced sustainable biomaterials because their properties are enhanced following the incorporation of the fillers. In the case of smart conventional GIC restorative materials, while they demonstrated fluoride release and excellent thermal performance within the oral cavity, they also exhibited thermal contraction and expansion that was not in line with the natural tooth structure. The discrepancy between these materials and the natural tooth structure is a persistent problem, as it can cause interfacial stress, which in turn may result in microleakage [8].

Conventional guaranteed investment contracts undergo minimal dimensional alterations when exposed to moisture, but they are susceptible to considerable shrinkage under dry conditions, particularly at high temperatures, at which 50° C facilitates its greatest shrinkage [9]. Similar to natural dentin, this behavior involves the absorption and release of moisture in response to environmental fluctuations [10]. In addition to the gel structural phase of conventional GIC, the other two significant phases of this material are cross-link and maturation structural phases. The cross-link structural phase of GIC is crucial for imparting hardness to the conventional GIC matrix after setting, while the maturation structural phase of GIC leads to changes in its physical, chemical, and mechanical properties. As a result, these structural phases within conventional GIC can compromise its structure at the tooth-restoration interface over time, ultimately resulting in the formation and spread of microcracks in its final form [9]. Over time, these small microcracks gradually expand and develop into larger macro-cracks due to heightened levels of solubility and brittleness. The eventual structural degradations in the smart conventional GIC compromised its durability, stability, and lifespan as well. The surface characteristics of conventional restorative materials allow for more active moisture infiltration into the restored tooth structure [10–12].

Recent studies have concentrated on altering the structure of traditional GICs with sophisticated nanoparticles in order to overcome these constraints, as shown in research [13]. Among these, titanium dioxide nanoparticles (Titania-NPs) have shown promising results due to their biocompatibility and enhanced antimicrobial properties, especially when synthesized from natural and environmentally friendly sources as they are cost effective, easily fabricated and more durable [14–17]. Previous studies have reported that commercially available TiO<sub>2</sub> NPs are bit more costly, harmful and cytotoxic to some extent [18,19]. In addition, these nanoparticles can alter the physical and chemical properties of restorative materials such as viscosity, size, stiffness, strength, shape, hardness, and damping, under the influence of a magnetic field, thermal conduction, and electrical conduction [20,21]. This can potentially overcome the limitations of conventional glass-ionomer cements, including microcracks and poor surface properties, thereby enhancing their durability and performance in the oral environment using natural materials [22]. Hence, these materials have become crucial in addressing numerous oral health issues.

It has been reported that nearly half of the world's population about 50 % is unable to acquire and maintain proper oral health conditions, with 3.8 billion people suffering from various oral diseases causing discomfort, disfigurement, and pain leading to death [23]. The primary oral health issues affecting individuals worldwide are caries, gingivitis, periodontitis, bone-related problems, and oral cancers [24], which collectively have a considerable impact on global health. Early detection and treatment of oral issues can be achieved using sustainable dental biomaterials, which can also cure and prevent these problems at their initial stages. In this regard, the American Society of Testing calls for the creation of cost-effective, sustainable, high-performance biomaterials that would be suitable for standard dental practices and uses, with the goal of enhancing oral health outcomes and overall quality of life [25], as also suggested by the American Society of Testing [26].

This study addresses the challenges by developing a cost-efficient and eco-friendly method for synthesizing new Titania nanoparticles

with corn silky fibers and then analysing and incorporating them into conventional Graphite Intercalation Compounds. The objective is to design a smart, Titania-enriched Glass Ionomer Cement (GIC) that not only satisfies clinical standards for shear bond strength and durability but also aims to produce a cost-efficient, marketable product for dental use.

## 2. Materials and methods

### 2.1. Synthesis

The locally sourced corn from Islamabad, Pakistan was obtained where Titanium tetra-isopropoxide sourced from Sigma Aldrich and meeting AR-grade standards with a purity of more than 97 % (CAS No: 546–68–9, supplied by Merck of Darmstadt, Germany) was used as a precursor in synthesizing the Nps. The Fibres taken from corn cob silky hair (SCHF - Stigma maydis) were thoroughly cleaned, dried, and divided into shorter fibre lengths of approximately 1–1.5 cm. A total of 20.0 g of these crushed SCHF were added to 100 mL of deionized water and the mixture was heated on metal plate at 60o C for about 10 minutes with vigorously continuous magnetic stirring. The resulting extract solution was then filtered using Whatman filter paper and stored for future synthesis in a refrigerator at 4 °C. A solution of 10 mL of SCHF extract was mixed with 100 mL of 0.1 M Titanium tetra-Isopropoxide under constant magnetic stirring of 600 rpm at room temperature for 24 hours. A color change from yellowish-brown to white was observed to indicate the formation of TiO<sub>2</sub> NPs. The NPs were then thoroughly washed several times with deionized water and ethanol, employing centrifugation for the washing process. The NPs crystals were dried and heat-treated at 110 degrees Celsius for 4 hours [27].

### 2.2. Characterization

The synthesised TiO<sub>2</sub> NPs were investigated using multiple analytical methods to identify their crystalline structure, dimensions, morphology, surface properties, chemical functionality, and elemental makeup [27]. The following equipment was utilized: an x-ray diffraction (XDR) instrument (DPP-MAX-Z 2400-Diffractometer, Rigaku Corporation, Akishima, Tokyo, Japan); a combination of scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDS) with equipment consisting of a Nova nanosem 4300, FEI company with serial number 4022 261 493910, column setup F/G strong prep, Hillsboro, OR, USA); Fourier transform infrared spectroscopy (FTIR) using a JASCO-1 FTIR-6600, Utrecht, Amsterdam, Netherlands; atomic force microscopy (AFM) employing a Quesant-z Universal SZM, Ammbios Technologies, Santa-Cruz, CA, USA; and dynamic light-scattering (DLS) with a Zeta Sizer-Nano Z/S Apparatus, model number ZENS-36000, Malvern-analyticals in Malvern, United Kingdom. The crystalline size and phase of TiO<sub>2</sub> nanoparticles were determined by analyzing the diffraction pattern, which was plotted as intensity against Bragg's angle (2θ), using Bragg's law ( $n\lambda = 2d\sin\theta$ ) in X-ray diffraction (XRD). A conductive gold coating was created after passing a focused electron beam through NPs, which then produced high-resolution images in the SEM, providing detailed information about the surface and texture of these NPs. The EDX segment in the SEM was employed to verify the elemental composition of the specific elements present within the NPs via the electron beam emitted. The functional groups were examined using FTIR by comparing the spectrum peaks corresponding to distinct vibrations, which were generated through infrared light absorption by the sample, with standard IR-spectrum data. TiO<sub>2</sub> NPs were secured to a glass slab, and a cantilever tip in tapping mode was utilised in the AFM to produce a 3D scan texture of the surface, which revealed the smoothness or roughness of these NPs. The hydrodynamic size was shown to be consistent with the Stokes-Einstein equation, as evidenced by fluctuations in the light scattered by a laser beam in dynamic light scattering (DLS).

### 2.3. Incorporation of TiO<sub>2</sub> NPs in GIC powder

Various concentrations of TiO<sub>2</sub> NPs were combined with GC universal restorative cement 2 using a vortex mixer for at least one minute to achieve a uniform dispersion as per the standard protocol because this time duration of mixing was enough for getting the homogenously mixed TiO<sub>2</sub> NPs into GC powder. The concentrations employed in this research comprised 0 % (Conventional GIC), Smart Titania-GIC at 3 %, Smart Titania-GIC at 5 %, Smart Titania-GIC at 7 %, and Smart Titania-GIC at 10 % in order to avoid variability in the results [28]. The composition of 0 % conventional GIC consisted of 0 g of TiO<sub>2</sub> NPs and 5 g of conventional GIC powder. In contrast, the quantities of TiO<sub>2</sub> NPs and conventional GIC powder incorporated in Smart Titania-GIC at 3 % concentration were 0.15 g and 4.85 g, while in the 5 % concentration it was 0.25 g and 4.75 g, in the 7 % concentration it was 0.35 g and 4.65 g, and in the 10 % concentration it was 0.50 g and 4.50 g respectively. Blocks of conventional glass-ionomer cement and TiO<sub>2</sub>-enriched glass-ionomer cement were prepared using metal molds measuring 4 × 4 × 1 mm, with various concentrations examined in this study, including 0 % conventional GIC, and Smart Titania-GIC at 3 %, 5 %, 7 %, and 10 % titania concentrations. Blocks were produced using the specified molds, which measured 4 × 4 × 1 mm, in accordance with the manufacturer's guidelines to facilitate the examination of spectrum mapping for compositional analysis, enamel shear bond strength and surface morphological analysis [28].

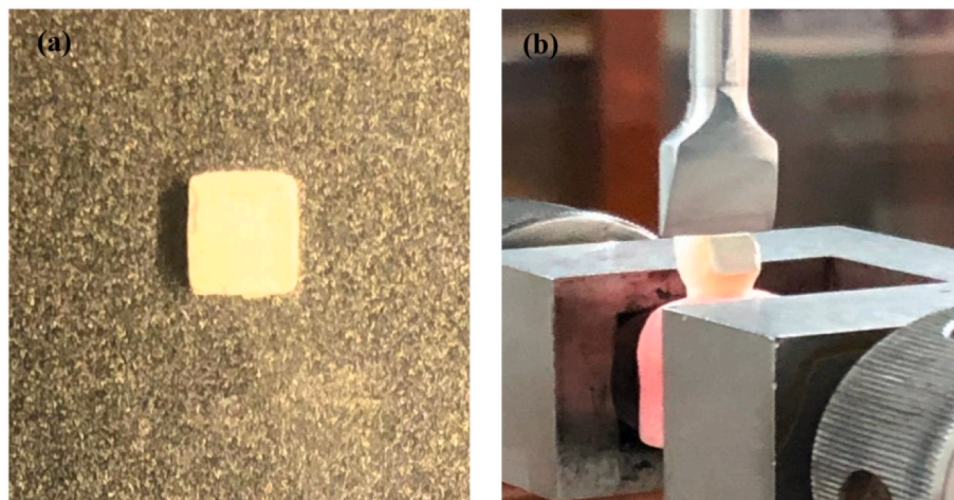
### 2.4. Spectrum mapping for compositional analysis

Blocks of conventional glass-ionomer cement and TiO<sub>2</sub>-enriched glass-ionomer cement at varying concentrations, including 0 % conventional GIC, Smart Titania-GIC at 3 %, 5 %, 7 %, and 10 %, were polished using 400 and 800 grit silicon carbide paper on a metallographic polishing machine from Nanjing Scientific Instrument Measurement & Control Co; Ltd. The gold-coated blocks were then secured to an aluminium stub for the purpose of conducting spectrum mapping for compositional analysis using the SEM with EDS on the pre-treated samples, specifically with the Nova nanosem 4300 system from FEI company (columns F/G strong preps, 4022 261 493910-s, Hillsboro, OR, USA) as referenced in literature [28].

### 2.5. Enamel shear bond strength testing

This study utilised a total of 100 human anterior teeth that had been recently extracted and were loose due to periodontal disease. Extracted anterior teeth without cracks, caries, lesions, or restorations were included in this study, whereas those with these issues were excluded. The samples were preserved in a 0.1 % thymol solution prior to further analysis. The teeth were categorized into five distinct groups, each consisting of 20 samples, according to the varying concentrations of GIC: conventional GIC, TiO<sub>2</sub>-GIC at 0 %, 3 %, 5 %, 7 %, and 10 %. The labial surfaces of all teeth were polished with 400 and 800 grit silicon carbide abrasive paper on a metallographic polishing machine, specifically one manufactured by the Nanjing Scientific, Instrument Measurement & Control Co; Ltd. The teeth were then submerged in epoxy resin, exposing and positioning the labial enamel surfaces for shear bond strength analysis in a Universal Testing Machine under controlled room temperature conditions as prescribed by standard procedure [27]. The 4x4x1 mm blocks of Conventional GIC and different TiO<sub>2</sub>-GIC groups were bonded to the enamel labial surfaces and cleaned using an ultrasonic cleaning machine (Branson; Smith Kline Company; USA) for one minute. Shear bond strength testing was conducted using a universal testing machine (Shenzhen SANS: Testing Machine Co; Ltd. China) at a cross-head speed of 1 mm/min until the bond between the blocks and enamel surfaces got detached. The maximum force required to debond each block was recorded and used to calculate the shear bond strength which was according to the standardized protocols of ISO 29022:2013 (Fig. 1)





**Fig. 1.** Illustrates the procedure for preparing anterior teeth embedded in epoxy resin (a), and the detachment of a TiO<sub>2</sub>-GIC block from an anterior tooth during enamel shear bond strength testing on a universal testing machine as per standardized protocol (b).

[29].

## 2.6. Surface morphological analysis

The enamel shear bond strength testing involved separating the blocks of both conventional glass ionomer cement (GIC) and TiO<sub>2</sub>-GIC blocks from their initial attachment to the labial surfaces of human anterior teeth. The dislodged blocks of conventional GIC and TiO<sub>2</sub>-GIC were coated with carbon using the sputter-coating method and subsequently attached to an aluminium stub used within the SEM equipment Nova nanosem 4300 model operated by FEi company, with column references F/G strons, Hillsboro, OR, USA, under the company registration number 4022 261 493910. The electronic beam was used to examine the surface morphology and texture, as indicated in reference [28].

## 2.7. Statistical analysis

The data was analyzed using IBM SPSS software, version 24.00, developed by IBM Corporation, which is headquartered in Armonk, CA, USA. A one-way analysis of variance was used to compare the average enamel shear bond strengths of various glass ionomer cement formulations. Post-hoc Tukey's tests were employed to examine the differences between groups, with a predetermined level of significance of less than  $p < 0.05$ .

## 3. Results

### 3.1. Synthesis of titania nanoparticles (TiO<sub>2</sub> NPs)

The successful synthesis of TiO<sub>2</sub> NPs was verified by a noticeable color shift in the SCHF solution, which changed from light cream to white, and was accompanied by the formation of solid particles within the container.

### 3.2. Characterization of TiO<sub>2</sub> NPs

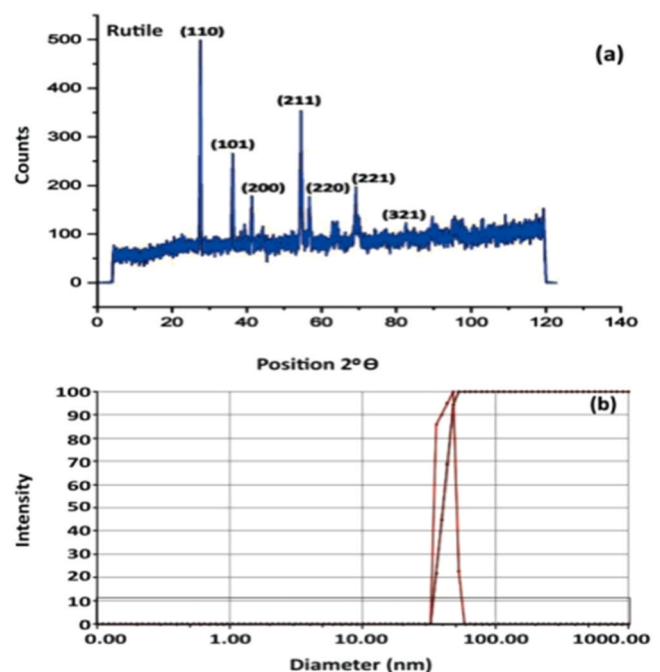
#### 3.2.1. Phase-form and particle size analysis

X-ray diffraction analysis was used to identify the phase and diameter of SCHF based titanium dioxide nanoparticles which matched file number 01-078-1510. The X-ray diffraction pattern showed the rutile phase, with the main peak observed at  $2\theta = 27.58^\circ$  corresponding to the (110) plane. New peaks were detected at  $2\theta$  angles of  $36.25^\circ$  (101),  $39.39^\circ$  (200),  $54.47^\circ$  (211),  $56.80^\circ$  (220),  $65.68^\circ$  (221), and  $82.58^\circ$

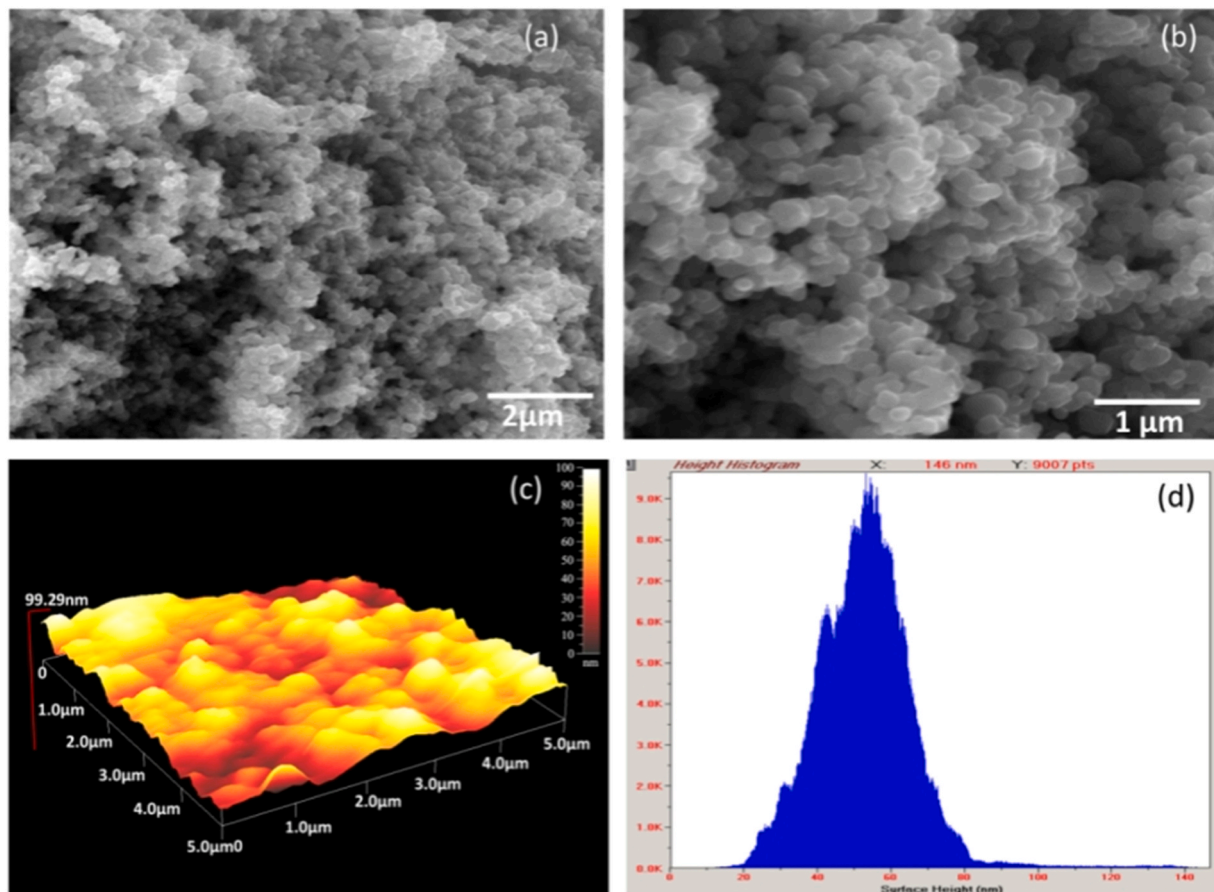
(321), thereby verifying the 100 % pure rutile phase of the nanoparticles. The Debye-Scherrer's formula was employed to determine the particle size, which was discovered to be 24.17 nm, as depicted in Fig. 2a. The particle size of the hydrodynamic analysis, as measured by dynamic light scattering (DLS), was found to be 35.31 nanometers, with a standard deviation of 0.170, suggesting a slight rise in particle size resulting from aggregation in solution. Confirmation readings were taken on three separate occasions (Fig. 2b).

#### 3.2.2. Surface morphology analysis

Scanning electron microscopy images taken at 20,000x and 50,000x magnifications showed that the titanium dioxide nanoparticles were spherical in shape (Fig. 3a, b). Atomic force microscopy scans also confirmed the nanoparticles' smooth surface, with only a minimal level of roughness detected in the three-dimensional scans (Fig. 3c, d).



**Fig. 2.** Illustrates the phase form of SCHF TiO<sub>2</sub> NPs, which exhibit a rutile phase in the XRD pattern (a), and their hydrodynamic size, which shows larger particle sizes in the DLS scan (b).



**Fig. 3.** Scanning Electron Micrographs of SCHF  $\text{TiO}_2$  NPs exhibit spherical morphology (a, b), while Atomic Force Microscopy scans reveal a smooth surface with minimal surface roughness (c, d).

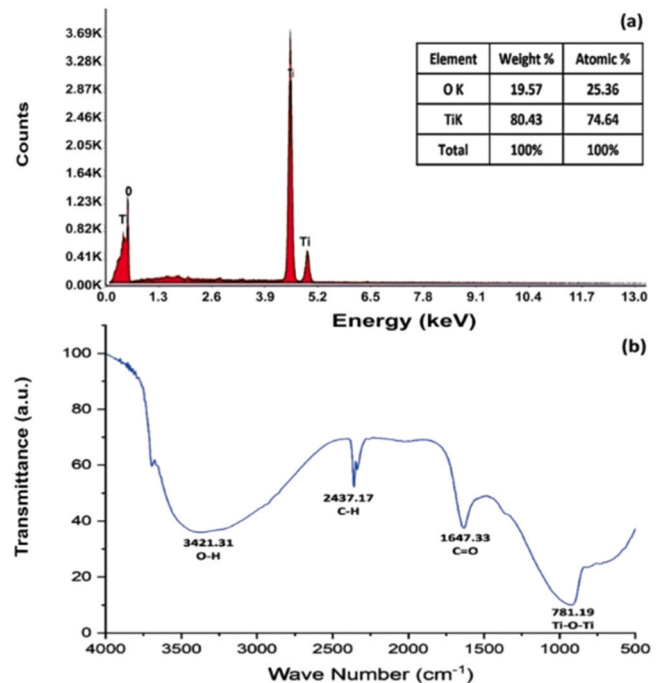
### 3.2.3. Elemental composition and functional compound analysis

EDX confirmed the elemental composition of the SCHF-based  $\text{TiO}_2$  NPs, with titanium and oxygen being the predominant elements, with titanium and oxygen being the predominant elements, accounting for 80.43 % by weight and 74.64 % by atomic percentage for titanium, and 19.57 % by weight and 25.36 % by atomic percentage for oxygen (Fig. 4a). FTIR identified key functional groups, including a strong O-H stretching vibration at  $3421.31 \text{ cm}^{-1}$  belonging to alcohol group, a C-H bending vibration at  $2437.17 \text{ cm}^{-1}$  belonging to aromatic compounds, amine groups at  $1647.33 \text{ cm}^{-1}$ , and a Ti-O-Ti bending vibration at  $781.19 \text{ cm}^{-1}$ , confirming the successful synthesis of  $\text{TiO}_2$  NPs (Fig. 4b).

### 3.3. Spectrum mapping for compositional analysis

Analysis of traditional GIC without titanium dioxide nanoparticles showed a distinct elemental composition, consisting of: 14.93 % carbon, 14.55 % oxygen, 2.04 % fluorine, 23.95 % aluminium, 20.07 % silicon, 22.60 % strontium, 1.70 % phosphorus, and 0.16 % sulphur. The highest concentrations of Al, Sr, Si, C, and O were detected, with F, P, and S present in significantly lower amounts as shown in Table 1. Elemental mapping confirmed the presence of carbon, oxygen, fluorine, aluminum, silicon, strontium, phosphorus, and sulphur (Fig. 5a).

When  $\text{TiO}_2$  NPs were introduced into the GIC matrix at varying concentrations (3 %, 5 %, 7 %, and 10 %), compositional changes were observed. The compositional analysis of smart Titania-GIC (3 %) demonstrated the presence of C (13.57 %), O (15.91 %), Al (23.89 %), Si (20.03 %), Sr (21.19 %), P (1.17 %), S (0.15 %), F (3.59 %) and Ti (0.50 %). The amounts of Al, Sr, Si, C, O, P and S were reduced whereas F was increased in comparison to the Conventional GIC. Notably, the presence of titanium (0.50 %) was confirmed (Table 1). The presence of



**Fig. 4.** Analysis of the elemental composition of SCHF  $\text{TiO}_2$  NPs revealed peaks corresponding to titanium and oxygen in its EDX spectrum, as shown in (a). Additionally, functional group analysis of SCHF Titania Nps demonstrated peaks for various functional groups, as illustrated in (b).

**Table 1**Composition in terms of weight/weight percentage of elements in a conventional GIC (0 %) and varying concentrations of Smart  $\text{TiO}_2$  NPs -GIC.

| Ser   | Elements | Conventional - GIC (0 %) | Smart Titania-GIC (3 %) | Smart Titania-GIC (5 %) | Smart Titania-GIC (7 %) | Smart Titania-GIC (10 %) |
|-------|----------|--------------------------|-------------------------|-------------------------|-------------------------|--------------------------|
| 1.    | Al       | 23.85                    | 23.79                   | 23.33                   | 22.03                   | 20.92                    |
| 2.    | Si       | 20.02                    | 19.99                   | 20.55                   | 20.07                   | 19.58                    |
| 3.    | C        | 14.23                    | 13.01                   | 11.25                   | 12.73                   | 13.05                    |
| 4.    | O        | 14.45                    | 15.71                   | 15.23                   | 10.60                   | 12.13                    |
| 5.    | F        | 1.99                     | 3.35                    | 6.43                    | 9.93                    | 10.17                    |
| 6.    | Sr       | 22.57                    | 21.23                   | 20.22                   | 19.97                   | 19.23                    |
| 7.    | P        | 1.73                     | 1.13                    | 0.34                    | 0.95                    | 0.57                     |
| 8.    | S        | 0.19                     | 0.17                    | 0.11                    | 0.29                    | 0.15                     |
| 9.    | Ca       | 0.41                     | 0.37                    | 0.29                    | 0.35                    | 0.39                     |
| 10.   | Na       | 0.56                     | 0.72                    | 1.44                    | 1.11                    | 1.32                     |
| 11.   | Ti       | 0                        | 0.53                    | 0.81                    | 1.97                    | 2.49                     |
| Total |          | 100                      | 100                     | 100                     | 100                     | 100                      |

carbon, oxygen, fluorine, aluminum, silicon, strontium, phosphorus, sulphur and titanium were revealed in its composition by the elemental spectrum mapping (Fig. 5b).

The compositional analysis of a 5 % smart Titania-GIC revealed its atomic composition to comprise 12.03 % carbon (C), 16.21 % oxygen (O), 6.46 % fluorine (F), 23.51 % aluminium (Al), 20.01 % silicon (Si), 20.57 % strontium (Sr), 0.33 % phosphorus (P), 0.09 % sulphur (S) and 0.79 % titanium (Ti). Compared to the conventional-GIC and smart titania-GIC group (3 %), the levels of Al, Sr, Si, P, and S decreased, whereas F and Ti levels increased. The greatest reduction in carbon content and the largest increase in oxygen levels were seen in this particular group as shown in Table 1. The elemental spectrum mapping (Fig. 5c) revealed the presence of carbon, oxygen, fluorine, aluminum, silicon, strontium, phosphorus, sulphur, and additional titanium in its composition.

The elemental composition of the smart Titania-GIC was found to consist of carbon (13.55 %), oxygen (10.51 %), fluorine (10.30 %), aluminum (22.02 %), silicon (20.00 %), strontium (20.41 %), phosphorus (0.97 %), sulfur (0.31 %), and titanium (1.93 %) in atomic percentage, as determined by compositional analysis. Compared to conventional GIC and smart Titania-GIC (3 %), the levels of Al, Sr, Si, P, S and C were decreased, whereas F and Ti were increased even more. In comparison to the smart Titania-GIC (5 %), the group's content of P, S, C, and F was higher, whereas O, Al, Sr, and Si were present in lower concentrations (Table 1). The elemental composition, which includes carbon, oxygen, fluorine, aluminum, silicon, strontium, phosphorus, sulphur and titanium, was verified by elemental spectrum mapping in its composition (Fig. 5d).

The compositional analysis of a 10 %  $\text{TiO}_2$  NPs-GIC composition revealed the elemental constituents to be 13.02 % carbon, 14.01 % oxygen, 10.34 % fluorine, 20.62 % aluminium, 19.71 % silicon, 19.14 % strontium, 0.59 % phosphorus, 0.11 % sulfur, and 2.45 % titanium. In comparison to Conventional-GIC, smart Titania-GIC (3 %) and smart Titania-GIC (7 %), the levels of Al, Sr, Si, P, S and C were decreased, whereas F and Ti levels were increased even further. The concentration of elements P, S, C, and F in this group exceeded that of smart Titania-GIC (5 %), whereas O, Al, Sr, and Si were present in lower amounts compared to the others (Table 1). Confirmation of carbon, oxygen, fluorine, aluminium, silicon, strontium, phosphorus, sulphur, and titanium in its composition was achieved through elemental spectrum mapping (Fig. 5e).

### 3.4. Enamel shear bond strength testing

The study of enamel shear bond strength found a non-linear connection with rising Titania NP concentration within the GIC. The strongest shear bond was achieved with the 5 % smart Titania-GIC, which had a mean value of  $4.93 \pm 0.74$  MPa (standard error = 0.23). Conversely, the weakest shear bond was observed in the 10 % smart Titania-GIC with a mean value of  $3.44 \pm 0.57$  MPa (standard error = 0.18). Significant improvements were also observed at intermediate

concentrations of 3 % and 7 % compared to the conventional GIC, with enhancements of  $2.17 \pm 0.20$  S. Shear bond strengths were  $2.99 \pm 0.45$  MPa and  $3.96 \pm 0.30$  MPa as indicated in Fig. 6 with a corresponding value of  $E = 0.06$ . The shear bond strength values were elaborated in unit of MPa for better understanding. Analysis of the data revealed a statistically significant distinction between the groups, with a probability value of less than 0.05.

The statistically significant disparity in the mean values between SCHF Titania-GIC at varying percentages and conventional GIC was also observed at a significance level of less than 0.05 (Table 2).

### 3.5. Surface morphological analysis

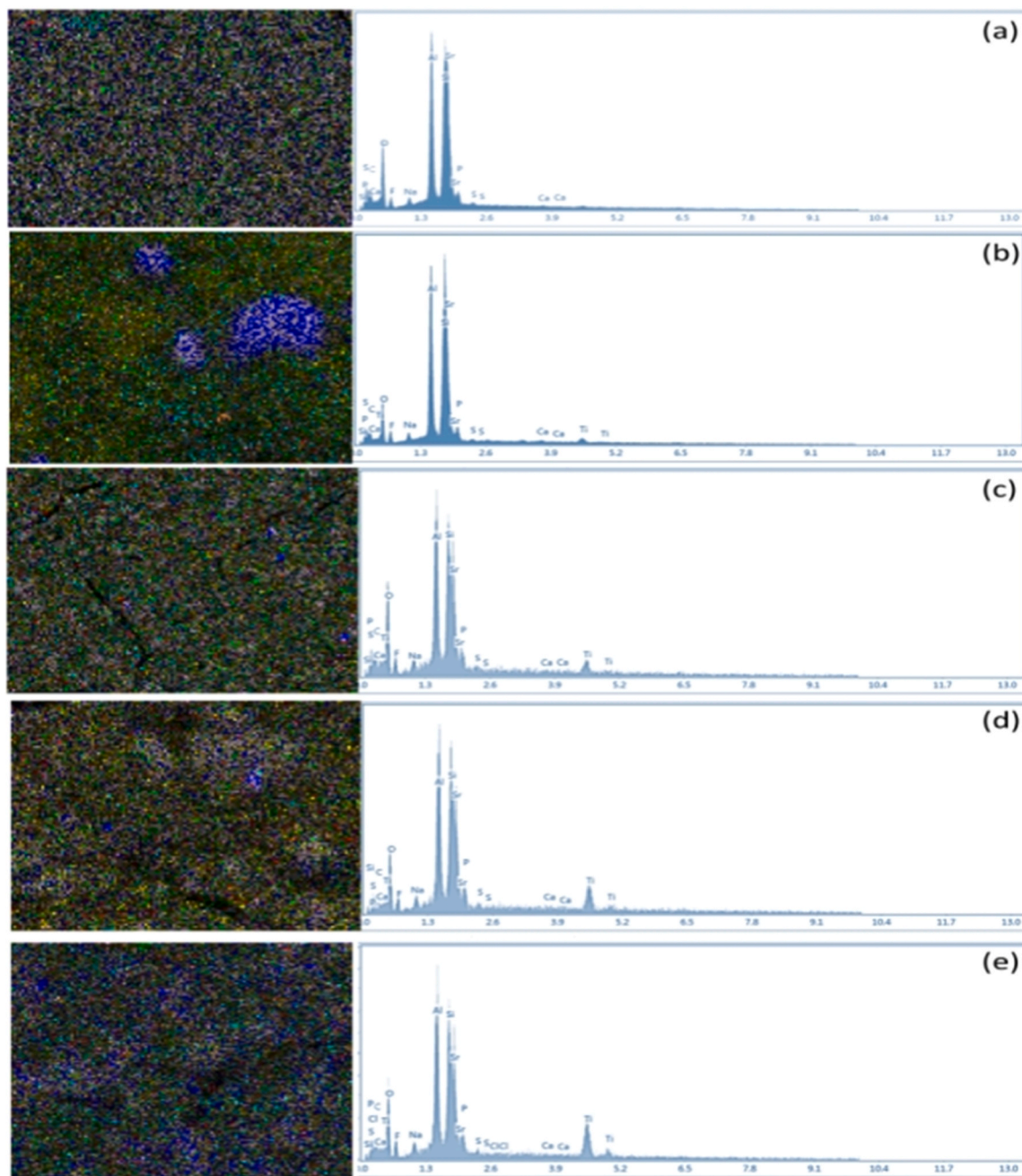
SEM analysis of the surface morphology revealed that conventional GIC particles were larger with noticeable surface cracks, voids, and disintegration sites (Fig. 7a,b). As Titania NP concentration increased, these surface defects gradually decreased, reaching a minimum at 5 % Titania-GIC (Fig. 7c, d, e, f). However, at higher concentrations (7 % and 10 %), the surface defects began to increase again, suggesting an optimal concentration of Titania NPs at 5 % for minimizing surface imperfections (Fig. 7g, h, i, j).

## 4. Discussion

GIC is widely accepted within restorative dentistry for its varied and advantageous characteristics, including its strong bonding to tooth structure, caries-preventing properties resulting from fluoride release, biocompatibility, and compatibility with dentin in terms of elasticity and thermal expansion. A notable disadvantage of GIC is its compromised mechanical properties and decreased shear bond strength to both enamel and dentin, which is commonly linked to the development of voids and air entrapment within its structure [30]. The voids in the material differ in terms of size and quantity, which can lead to areas of high stress that threaten the material's structural integrity. Recent advancements in nanotechnology have introduced nanoparticles as a promising solution to these issues. This study centered on the synthesis of environmentally friendly  $\text{TiO}_2$  nanoparticles via the use of SCHF. The resulting nanoparticles were identified as being in the rutile phase with spherical shapes, having smooth surfaces and elemental and functional group compositions ranging from 19 to 24 nm, all of which are favourable for boosting the shear bond strength of conventional glass ionomer cement to enamel (Figs. 1–6).

Previous studies emphasize that size, shape, surface texture, and state of nanoparticles (NPs) are critical factors influencing their performance in medical and dental contexts, particularly those of titanium dioxide ( $\text{TiO}_2$ ) NPs derived from natural sources in the environment. The naturally derived sources used for the fabrication of  $\text{TiO}_2$  NPs are cost effective, eco-friendly and bio-safe in nature [31,32]. The specified parameters, in conjunction with the synthesis process, are responsible for the stability and operational efficiency of NPs [32–34]. The  $\text{TiO}_2$  NPs synthesised in this study showed a high level of purity and stability,



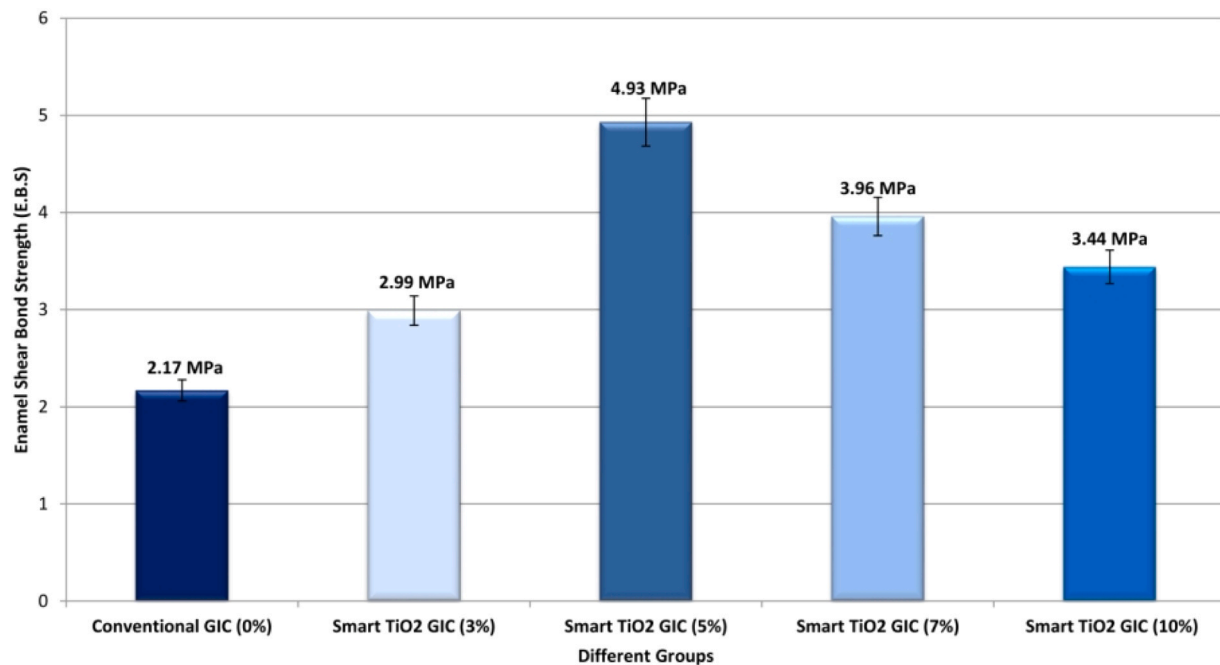


**Fig. 5.** Conventional glass ionomer cement and smart  $\text{TiO}_2\text{NPs}$ -GIC were mapped using spectrum analysis at different concentrations for compositional evaluation, showing: (a) the composition of conventional GIC (0 %) as a percentage of elements in the EDX spectrum, (b) Smart Titania-GIC (3 %) composition as a percentage of elements in the EDX spectrum, (c) Smart Titania-GIC (5 %) composition as a percentage of elements in the EDX spectrum, (d) Smart Titania-GIC (7 %) composition as a percentage of elements in the EDX spectrum, and (e) Smart Titania-GIC (10 %) composition as a percentage of elements in the EDX spectrum.

primarily due to the natural biomolecules found in the SCHF, which facilitated the production of nanoparticles with these desirable characteristics. Surface morphology analysis of the GIC samples showed significant variations across different formulations. A conventional GIC without  $\text{TiO}_2$  NPs displayed particle size and highly porous structure, characterised by numerous voids, cracks, and disintegration sites, as evident in Fig. 7a and b. In contrast, incorporating  $\text{TiO}_2$  NPs in smart Titania-GIC at a concentration of 3 % revealed particle size and led to a noticeable decrease in these defects, as shown in Figs. 7c and 7d. The particle size and reduction in defects was even more significant in the smart Titania-GIC with a concentration of 5 %, as seen in Figs. 7e and 7f. However, the defects started to increase in the smart Titania-GIC with a concentration of 7 % with particle size (Figs. 7g and 7h) and were most

apparent in the smart Titania-GIC with a concentration of 10 % with particle size (Figs. 7i and 7j).

A flat surface in morphology is a vital necessity for any perfect restorative material utilised in clinical dentistry, as it boosts mechanical properties, shear bond strength and prevents caries progression [35,36]. The surface quality of traditional glass-ionomer cement is compromised by a number of factors, specifically dehydration, moisture sensitivity, and the setting time. The compositional features within the matrix of conventional-GIC powder particles have also been considered to be the cause of a decline in its enamel shear bond strength. Additional factors influencing the process include particle-particle interfacial bonding, particle-matrix interfacial bonding, storage conditions, powder particles, the powder-to-liquid ratio, particle count, and their aggregation,



**Fig. 6.** Comparison of enamel shear bond strength (E.B.S) to conventional glass ionomer cement (GIC) and smart Titania-GIC at various concentrations. Differences in enamel shear bond strength (E.B.S) to conventional GIC and smart Titania-GIC at different concentrations.

distribution, dimensions, and morphology [35,36]. Conventional GICs' large particle size results in air entrapment during mixing, which causes the formation of voids that negatively impact both the structural morphology, mechanical properties and shear bond strength of the final matrix. These voids provide a route for fluids and microorganisms to penetrate, thereby facilitating plaque development, the formation of secondary caries, and ultimately structural deterioration [37].

The TiO<sub>2</sub> nanoparticles produced in this research, characterised by their small dimensions, even surface, and high level of purity, effectively filled the voids in the conventional-GIC powder, thereby enhancing the stability of the structural morphology and enamel shear bond strength. The incorporation of these non-porous surfaces also enhanced the smoothness of the glass-ionomer cement surface, which may lower bacterial adherence and enhance the material's overall efficiency. Analysis of composition and mapping of elemental spectra demonstrated a linear decline in the concentrations of aluminium, silicon, strontium, phosphorus, carbon, and sulphur across the experimental groups as shown in Fig. 5a. The contents of Ca, Na, F, and Ti increased linearly from the conventional GIC (0 %) (Fig. 5a) to the smart Titania-GIC (10 %) (Fig. 5e). In contrast, the smart Titania-GIC (5 %) showed a slight decrease in the contents of Al, Si, and Sr, with the greatest decline observed in C, P, and S. In contrast, this group exhibited a maximum increase in oxygen content and an intermediate increase in calcium, sodium, and fluorine content, as shown in Fig. 5c. The modifications in elemental composition indicate that the addition of the newly synthesised TiO<sub>2</sub> nanoparticles changes the material's structure, which may increase its enamel shear bond strength and stability.

A thorough compositional analysis and spectrum mapping are essential for a proper understanding of any oral material used in clinical dentistry because these features might be helpful in enhancing the shelf life and stability of the smart innovative restorative material fabricated in the current study. The distribution of elements on the external surface of dental material is accurately depicted as coming into close contact with oral tissues. A limited number of studies have found that the structural, biological, physical, chemical, and mechanical properties of dental materials are heavily influenced by the presence of various elements within their chemical makeup [28,38]. The current study found that the conventional Gold GIC- Universal 2 has the same fundamental

elemental makeup as that found in research using commercial FAX-II GIC, which is consistent with existing literature [28,35]. A study led by Zanata et al [39]. found that the major components of GIC were aluminium (16.900 %), silicon (15.800 %), fluorine (5.100 %), phosphorus (2.700 %), calcium (3.700 %), strontium (11.100 %), and another form of phosphorus (1.100 %), as reported in reference. The variation in the basic composition of commercially available conventional-GIC can be attributed to the manufacturer's guidelines.

The conventional-GIC's stability is attributed to the presence of aluminium and silicon in its set matrix [40]. The aluminum content in both the conventional-GIC and smart Titania-GIC (containing 5 % Titania) samples in this study was approximately equivalent, whereas the silicon content in the smart Titania-GIC samples was slightly higher compared to the control group and other experimental groups. The achievement of this outcome could be attributed to effective distribution of the powder, enabling accurate aggregation between particles of GIC and 5 % smart Titania, thereby enhancing its stability.

Calcium and phosphorus in GIC are notable for enhancing shear bond strength to some degree, however, elevated levels compromise both strength and appearance by reducing radiopacity. Incorporating barium, strontium, and lanthanum into GIC as optic modifiers may address aesthetic concerns, however, these elements have been associated with inducing genotoxic and cytotoxic effects [41]. Our research indicated a small decrease in Ca and P levels in smart Titania-GIC (5 %), which might be attributed to the higher quantities of basic components. These elements would have contributed to the stability of the smart material, while also enhancing the particle-matrix and particle-particle interfacial bonding of the innovative restorative material through strong approximation.

Conventional glass-ionomer cements generally contain fluoride, which helps prevent recurring caries attacks by improving their shear bond strength, albeit to a limited degree. The fluoride release from GIC restorations in the oral cavity should persist throughout a person's lifetime. The product should be launched in a highly regulated manner due to its efficacy in reducing the occurrence of secondary or recurrent caries. In conventional-GIC, the release of fluoride is typically regulated by factors including particle size, powder-to-liquid ratio, pH levels, and primary elemental composition [42,43]. A study found that prolonged



**Table 2**

Comparisons were made between the shear bond strength of enamel and conventional glass ionomer cement, as well as various concentrations of smart Titania-glass ionomer cement.

| Conventional GIC and different concentrations of smart Titania-GIC Samples | Comparison of enamel shear bond strength (MPa) between conventional GIC and different concentrations of smart Titania-GIC samples | Mean Difference of enamel shear bond strength (MPa) between conventional GIC and different concentrations of smart Titania-GIC samples with Standard error (S.E) | p-value |
|--|---|--|---------|
| Conventional GIC (0 %)   | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (3 %)  | −0.82 (0.22)   | 0.003   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (5 %)  | −2.76 (0.22)   | 0.005   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (7 %)  | −1.79 (0.22)   | 0.002   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (10 %)   | −1.27 (0.22)   | 0.004   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (10 %)   | 0.82 (0.22)  | 0.003   |
| Smart TiO <sub>2</sub> GIC (3 %)   | Enamel shear bond strength to conventional GIC (0 %)  | −1.94 (0.22)   | 0.002   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (5 %)  | −0.97 (0.22)   | 0.001   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (7 %)  | −0.45 (0.22)   | 0.048   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (10 %)   | 2.76 (0.22)  | 0.005   |
|  | Enamel shear bond strength to conventional GIC (0 %)  | 1.94 (0.22)  | 0.002   |
| Smart TiO <sub>2</sub> GIC (5 %)   | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (3 %)  | 0.97 (0.22)  | 0.001   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (7 %)  | 1.49 (0.22)  | 0.001   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (10 %)   | 1.79 (0.22)  | 0.002   |
|  | Enamel shear bond strength to conventional GIC (0 %)  | 0.97 (0.22)  | 0.001   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (3 %)  | −0.97 (0.22)   | 0.001   |
| Smart TiO <sub>2</sub> GIC (7 %)   | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (5 %)  | 0.52 (0.22)  | 0.023   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (10 %)   | 1.27 (0.22)  | 0.004   |
|  | Enamel shear bond strength to conventional GIC (0 %)  | 0.450 (0.22)   | 0.048   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (3 %)  | −1.49 (0.22)   | 0.001   |
|  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (5 %)  | −0.52 (0.22)   | 0.023   |
| Smart TiO <sub>2</sub> GIC (10 %)  | Enamel shear bond strength to smart TiO <sub>2</sub> GIC (7 %)  |  |         |
|  |   |  |         |
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|  |   |  |         |

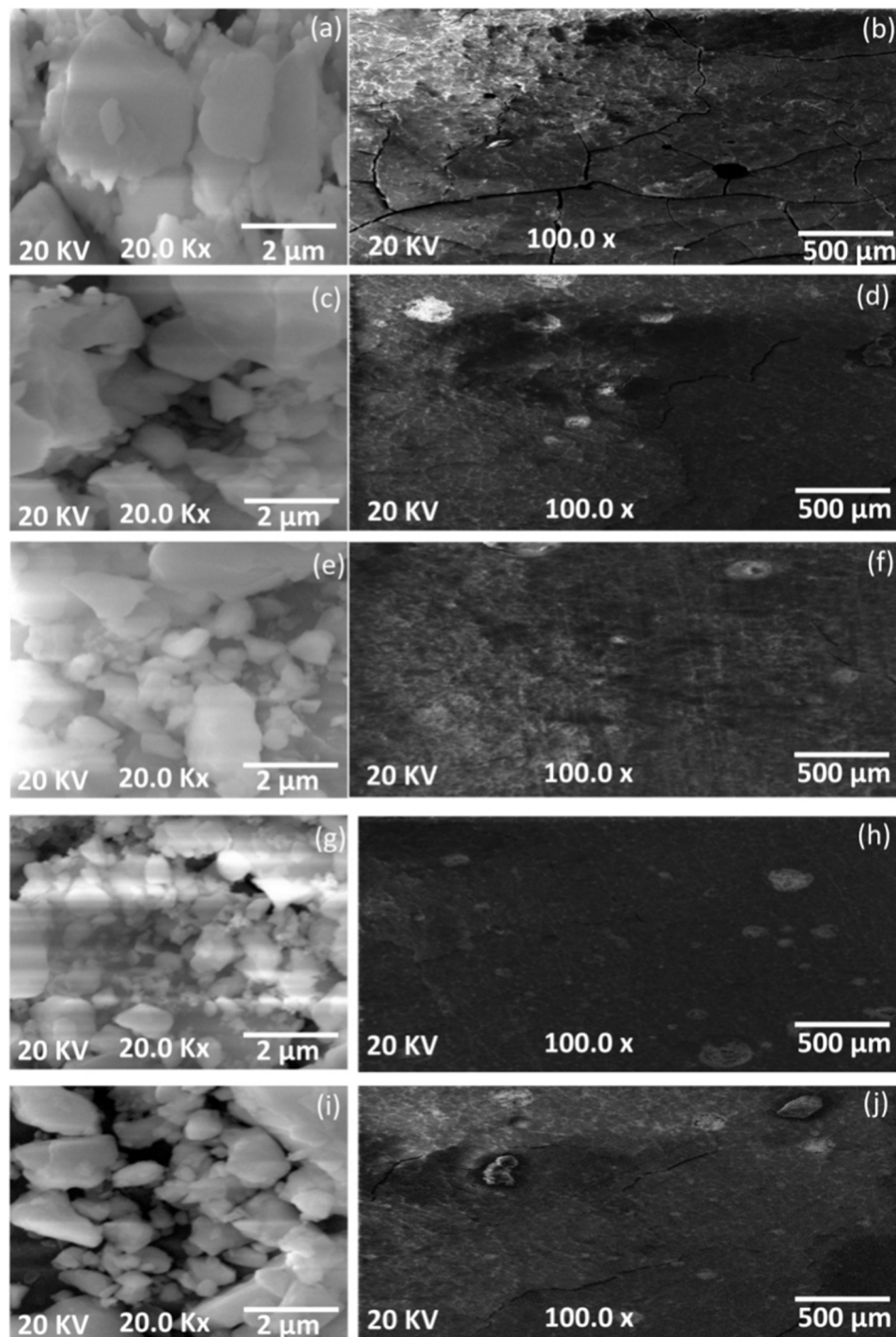
use of conventional-GIC in the mouth resulted in a decrease in fluoride content, which in turn weakened the material and led to the development of further tooth decay [35]. Researchers have found that adding commercially available nanoparticles to conventional-GIC increases its calcium and fluoride content [28,44], which could potentially mitigate issues with reduced strength and recurrent caries, but only up to a certain point. The notable increase in fluoride content, especially in the Titania-GIC at a concentration of 5 %, has the potential to prevent the formation of voids and cracks within the set matrix, ultimately enhancing enamel shear bond strength as illustrated in Fig. 6. Previous studies are supported by the compositional changes, which involve an increase in titanium (Ti) and oxygen (O), as well as a reduction in carbon (C). However, this alignment only applies to concentrations up to 5 % [28], as higher concentrations of 7 % and 10 % have not been studied. Studies also showed that incorporating commercially available Titania nanoparticles into conventional Glass-Ionomer Cement results in a decrease in Carbon content and an increase in Oxygen content on a small scale, caused by certain binding forces [45]. The small size, high purity, and stable rutile phase of these novel Titania nanoparticles in this study could have been synthesised in sufficient quantities to activate the strong interactive binding forces between the GIC-set matrix and NPs in the absence of any other by-product. The strong interactive forces between a matrix of large glass powder particles and smaller Titania nanoparticles could be the explanation for the improved shear bond strength of the enamel.

The Titania-GIC with a 5 % concentration showed the strongest enamel shear bond among all the tested samples, surpassing the conventional GIC with no Titania and other Titania-enriched formulations as shown in Fig. 5 and Table 1 [46]. These findings diverge from certain earlier research, which observed a less notable increase in shear bond strength with Titania NPs, likely owing to variations in nanoparticle stability and reactivity [28]. Their discovery could be attributed to the commercially available anatase Titania NPs experiencing unstable behavior due to their heightened reactivity, which permits moisture to penetrate the spaces between the conventional GIC matrix particles and NPs, resulting from the weak chemical bond between the glass and NPs. Titania NPs synthesised in the current study, which originated from a natural source with bioactive properties, displayed stable properties, resulting in stronger bonding interactions and thereby enhanced mechanical properties.

The structure of the tooth, chemical adhesion, and bonding are crucial factors in improving the shear bond strength of the enamel and preventing microorganisms from entering the set matrix of glass-ionomer cement restorations. Human tooth enamel consists of a uniform structure, primarily composed of hydroxyapatite with a high surface energy. The chemical reaction between phosphate ions in tooth enamel and carboxylate groups in liquid GIC is accountable for the chemical bonding between tooth enamel and conventional GIC [46]. The sustainable behavior of SCHF Titania NPs in smart Titania-GIC (5 %) may have allowed NPs in 5 % to react strongly with tooth enamel, resulting in changes to their structure, composition, and surface energy, which could have supported a chemical reaction that increased the shear bond strength to enamel up to a certain point. At a certain threshold, the chemical reaction could have become overly aggressive in an uncontrolled manner with an increase in the percentage of Titania NPs. Involvement of other smart Titania-GIC groups in this study could have resulted in adverse effects on their shear bond strength. Additional research is necessary to examine the outcomes of higher nanoparticle concentrations and to investigate the long-term durability and functionality of these advanced restorative materials within clinical environments.

## 5. Limitation

The main drawback of the present study is that a comparative analysis is required to evaluate the commercially available TiO<sub>2</sub> NPs



**Fig. 7.** Analysis by scanning electron microscopy was conducted on conventional glass ionomer cement and smart Titania-GIC at various concentrations, including the particle size and surface characteristics: (a,b) 0 % conventional GIC displaying particle size and largest number of voids, cracks, disintegration sites, (c,d) 3 % Smart Titania-GIC displaying particle size and slight decrease in number of voids, cracks, disintegration sites, (e, f) 5 % Smart Titania-GIC displaying particle size and maximum decrease in number of voids, cracks, disintegration sites, (g, h) 7 % Smart Titania-GIC displaying particle size and increase in number of voids, cracks, disintegration sites, and (i, j) 10 % Smart Titania-GIC displaying particle size and more increase in number of voids, cracks, disintegration sites in SEM micrographs.

and the newly synthesised TiO<sub>2</sub> NPs in terms of enamel shear bond strength. Additional research is needed to conduct a comprehensive analysis attributed to physico-chemical features of commercially available TiO<sub>2</sub> NPs versus the recently synthesised TiO<sub>2</sub> NPs in terms of their phase, size, shape, roughness, texture and morphology. Additional study is required to investigate the biological characteristics of this pioneering restorative substance in a controlled laboratory environment. Further research is also needed to study the entire mechanical properties of this

innovative and intelligent repair material in an in-vitro setting. Furthermore, the shelf life and stability of this smart material could be investigated via clinical trials in the future.

## 6. Conclusion

Researchers successfully produced environmentally friendly and long-lasting titania nanoparticles (TiO<sub>2</sub> NPs) utilizing silky corn hair

fibers (SCHF) as a natural raw material. The spherical nanoparticles displayed a smooth surface and a diameter of roughly 24.17 nm, with a majority of them being in the rutile form. The incorporation of these sustainable titania nanoparticles into glass ionomer cement at a concentration of 5 % resulted in a notable increase in enamel shear bond strength, surpassing that of standard glass ionomer cement formulations. Analysis of the material's structure showed that incorporating these nanoparticles successfully filled gaps and removed cracks and areas of disintegration within the GIC matrix. The 5 % titania-enriched GIC not only exhibits enhanced shear bond strength characteristics but also displays stability and durability, thereby making it a promising smart restorative material for dental applications. Further investigation is advisable to examine the long-term consequences and possible medical uses of this innovative material.

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## CRediT authorship contribution statement

**Afsheen Mansoor:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Emaan Mansoor:** Software, Methodology, Funding acquisition, Formal analysis. **Ezza Mansoor:** Writing – original draft, Funding acquisition, Formal analysis. **Efrab Mansoor:** Data curation, Formal analysis, Writing – original draft. **Atta Ullah Shah:** Methodology, Investigation, Data curation. **Uzma Asjid:** Methodology, Investigation, Formal analysis. **João Filipe Brochado Martins:** Writing – review & editing, Visualization, Validation. **Sami Ullah Khan:** Writing – review & editing, Validation, Supervision, Formal analysis. **Paulo Jorge Palma:** Writing – review & editing, Writing – original draft, Visualization, Validation.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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