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RESEARCH ARTICLE

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The influence of the addition of titanium oxide nanotubes on the properties of 3D printed denture base materials

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Abstract

Introduction: In this study, the effects of adding titanium dioxide nanotubes (TiO_2) to 3D-printed denture base resin on the mechanical and physical properties of denture bases were examined for the first time.

Methods: The specimens were digitally created using 3D builder software from Microsoft Corporation through computer-aided design. In accordance with the test specifications for transverse strength, impact strength, hardness, surface roughness, and color stability, specimens were designed and printed with certain dimensions following relevant standards. TiO_2 nanotubes (diameter: 15–30 nm and length: 2–3 μm) were added to the 3D-printed denture base resin (DentaBase, Asiga, Australia) at 1.0% and 1.5% by weight. Flexural strength, impact strength (Charpy impact), hardness, surface roughness, and color stability were evaluated, and the collected data were analyzed with ANOVA followed by Tukey's post hoc test ($\alpha = 0.05$). Field emission scanning electron microscopy (FESEM) and energy dispersive x-ray spectroscopy (EDX) mapping were used to evaluate the dispersion of the nanotubes.

Results: Compared with those of the control group (0.0 wt.% TiO_2 nanotubes), the average flexural, impact, and hardness values of the 1.0 and 1.5 wt.% TiO_2 nanotube reinforcement groups increased significantly. Both nanocomposite groups showed significant color changes compared to that of the pure resin, and there was a considerable reduction in the surface roughness of the nanocomposites compared to that of the control group.

Conclusion: Adding TiO_2 nanotubes to 3D-printed denture base materials at 1.0 and 1.5 wt.% could enhance the mechanical and physical properties of the material, leading to better clinical performance.

Clinical Significance: In terms of clinical applications, 3D-printed denture base material has been shown to be a viable substitute for traditional heat-cured materials. By combining this with nanotechnology, existing dentures could be significantly enhanced, promoting extended service life and patient satisfaction while addressing the shortcomings of the current standard materials.

KEYWORDS
3D printing, color stability, denture base resin, flexural strength, hardness, impact strength, titanium dioxide nanotube

1 | INTRODUCTION

Technological improvements in the health sector have led to longer life expectancies, and the aging population has increased worldwide.[1] One of the most prevalent oral health issues impacting the elderly population is complete edentulism.[2] Complete dentures remain the recommended option despite the availability of numerous treatment options.[3] The most popular resin in dentistry is polymethyl methacrylate (PMMA), which is employed because of its low density, aesthetic qualities, and affordability.[4] Nevertheless, the low mechanical and physical qualities of PMMA materials as well as the long fabrication time are major limitations of these materials.[5]

In dentistry, digital manufacturing technologies have become increasingly prevalent in the last several years. Currently available technologies for the manufacturing of removable dentures include computer-aided design and computer-aided manufacturing (CAD-CAM), which combines additive and subtractive techniques known as rapid prototyping and three-dimensional (3D) printing. Many users have tested the fast-evolving technology of 3D printing. Its rapid development can be attributed to the many benefits it offers over traditional approaches. It is sometimes referred to as the next industrial revolution's primary technology.[6,7]

The flexural strength and surface hardness of 3D-printed resins are lower than those of conventional and milled denture base materials;[8] nonetheless, the flexural strength approaches the 65 MPa mark, which is the ISO-accepted standard.[9] These drawbacks restrict the clinical applications of 3D-printed technology and make it difficult to use for denture base production.[10] Therefore, prior research has examined many aspects that impact the properties of 3D-printed resins, such as the printing orientation, postpolymerization time, and printing layer thickness, in an effort to overcome the aforementioned restrictions and gain the benefits of 3D printing technology.[11,12] According to Mangal et al.,[13] adding 0.1 wt.% nanodiamonds to 3D-printed resin improved its mechanical qualities for use in the creation of orthodontic appliances. Similarly, Aati et al.[14] demonstrated the long-term enhancement of a ZrO_2 nanoparticle (NP)-modified 3D-printed resin used for temporary restorations. Chen et al.[15] discovered that 3D-printable resin with two fillers, cellulose nanocrystals (CNCs) and silver nanoparticles (AgNPs), had improved mechanical and antibacterial properties. Nanofillers are effective fillers for composite resins; their high surface area and surface free energy have been demonstrated to increase the flexural strength of the resin.[16,17] According to Li et al.,[18] titanium oxide (TiO_2) nanotubes improve the mechanical properties of PMMA/composites because of their high specific surface area, strong metal support contact, superior chemical stability, and catalytic activity. Gad et al.[19] reviewed the effect of adding TiO_2 nanoparticles (NPs) to PMMA denture base materials to alter their properties. The enhancements in properties were predominantly observed at lower concentrations of TiO_2, while increasing the quantity of added nanoparticles led to adverse effects on the resulting PMMA/TiO_2 nanocomposite.

Several studies have investigated the alteration of 3D-printed materials using various additives. TiO_2 NPs improve the antibacterial capabilities of 3D-printed resins; however, their mechanical properties have not been examined.[20] The hardness, flexural strength, and fracture toughness of denture-based PMMA were successfully increased by the introduction of titanium nanotubes for the first time.[21] The incorporation of TiO_2 nanotubes into denture base PMMA resin has significant potential for enhancing its antimicrobial properties; hence, this material could be a promising candidate for manufacturing novel dental materials.[21] To the best of the authors' knowledge, no previous study has examined the effect or mechanical properties of TiO_2 nanotubes in combination with 3D-printed resin. The current study evaluated the effects of including TiO_2 nanotubes in 3D-printed resin. This study assessed the hardness, surface roughness, color stability, flexural strength, impact strength, and surface roughness of 3D-printed denture base resin following the addition of TiO_2 nanotubes. The initial null hypothesis assumed that the addition of TiO_2 nanotubes does not alter the properties of the 3D printed denture base resin.

2 | MATERIALS AND METHODS

2.1 | Materials and sample grouping

The denture base resin used to fabricate specimens by 3D printing was DentaBase (Asiga, Egypt, under ISO 13485:2016 & EN ISO 13485:2016), which is characterized by high strength and a natural pink color. According to the manufacturer's data sheet, the resin contains 7,7,9(or 7,9,9)-trimethyl-4,13-dioxo-3,14-dioxa-5,12-diazahexadecane-1,16-diyl bismethacrylate, tetrahydrofurfuryl methacrylate, and diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide. It should be noted that the manufacturer did not disclose any values for the mechanical or physical characteristics of the resin. TiO_2 nanotubes (Diameter: 15–30 nm; Length: 2–3 μm) were collected from Hongwu International Group, China, to create nanocomposites by mixing them with resin.

The amount of TiO_2 nanotubes used in this study was determined by a pilot study that tested the printability of a composite material with various TiO_2 nanotube percentages (1.0, 1.5, 2.0, 2.5, and 3.0 wt.%). Following the initial trials, 1.0 and 1.5 wt.% TiO_2 nanotubes were employed because the mechanical or physical characteristics dramatically decreased after the addition of 2 wt.% TiO_2. The sample size was calculated using the World Health Organization's formula, with the level of significance set at 0.05 and 80% power, which revealed that 10 specimens/group would provide reliable evidence. A total of 150 specimens were prepared according to the tests included

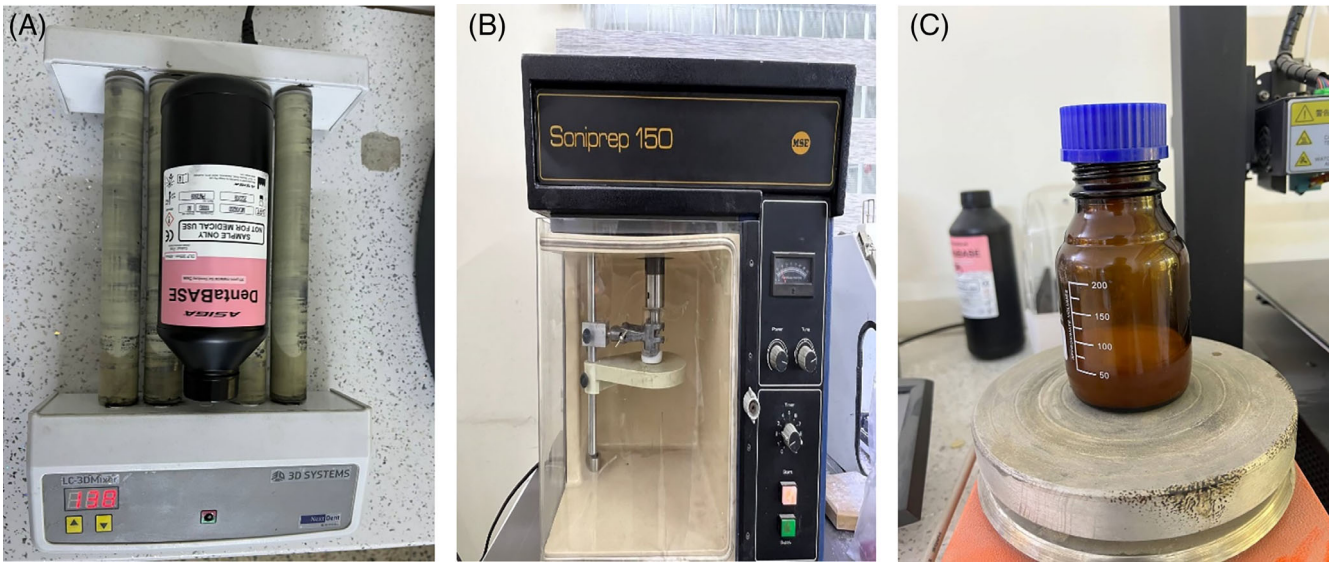

FIGURE 1 3D printing raw material preparation steps: (A) mixing of resin in a Mazic D mixer, (B) mixing of TiO_2 powder in ethyl alcohol with an ultrasonic probe, and (C) mixing of the resin and TiO_2 nanotubes using a magnetic stirrer.

in the study (flexural strength (30), impact strength (30), hardness (30), surface roughness (30), and color stability (30)). The specimens were divided into five groups based on the tests conducted. For each test, three subgroups were created, one for the control (pure resin) and two for TiO_2 nanotube percentages (1.0 and 1.5% wt.), as determined based on the results of a pilot study. Each subgroup contained 10 specimens to be tested.

2.2 | Sample Preparation

2.2.1 | Specimen Design

The specimens were digitally created using a 3D builder software from Microsoft Corporation through the application of computer-aided design. In accordance with the test specifications for flexural strength, impact strength, hardness, surface roughness, and color stability, the samples were designed with certain dimensions. The dimensions of the flexural test specimens, measured in accordance with ADA standard No. 12 (1999), were 65 × 10 × 2.5 mm. The impact strength test samples with dimensions of 80 × 10 × 4 mm were made in accordance with ISO 1791-1 specifications. As required by ADA standard No. 12 (1999), samples measuring 65 × 10 × 2.5 mm were produced for assessing surface roughness and hardness. A 20 mm diameter and 2 mm thick disc sample was prepared for color change testing. An average variations of ± 0.2 mm were recorded during the dimension measurements. Before testing, the edges and faces of all specimens were made smooth and flat via wet grinding using silicon carbide grinding papers at grain sizes of approximately 30 (P500), 18 (P1000), and 15 μm (P1200) sequentially to the required width and height. Prior to testing, all specimens were soaked in distilled water for a duration of 48 h, in accordance with ADA specification No. 12, 1999.

2.2.2 | Three-dimensional sample printing

A specific shaker (Mazic D mixer) was originally utilized to generate a uniform combination of basic resin for printing dentures. TiO_2 nanotubes (0.7 for 1.0 and 1.05 gm for 1.5 wt.%) and 3 mL of 99.9% ethyl alcohol were combined and mixed in an ultrasonic probe (MSE Soniprep 150, Netherlands) for 3 min to create a nanotube suspension, which was combined with denture base resin (70 gm) in a dark amber glass container that was covered to block out outside light. The mixture of denture base resin and TiO_2 nanotube suspension was mixed using an Alfa HS-860 magnetic stirrer for 30 min at 60°C and then allowed to settle at room temperature (25°C) for 8 h, as shown in Figure 1.

Digital light processing (DLP) 3D printer (Asiga, Australia) was used to print the specimens while maintaining the following settings: heater temperature = 30°C, high-power ultraviolet solid-state 385 nm LED, separation pressure limit = 300 g/cm^2, separation velocity = 4.3 mm/s, and layer thickness = 0.05 mm. To keep the liquid polymer combination (resin with titanium nanotube filler) out of the room light, the lid of the printer vat was closed after the mixture was added. The sample design was exported in STL format to be compatible for use with the printer's software. Upon projecting the light from the printer, the liquid resin started to solidify on the build platform due to polymerization. This procedure is carried out until the 3D model is completed. With a total of 30 samples to print, it took 40 min, and the layer construction proceeded in a horizontal manner. The sample was revealed by draining the liquid from the vat once it has solidified.

2.2.3 | Washing, drying, and postcuring

After completing the printing process, the samples were carefully removed from the 3D printer platform using a sharp knife. The printed

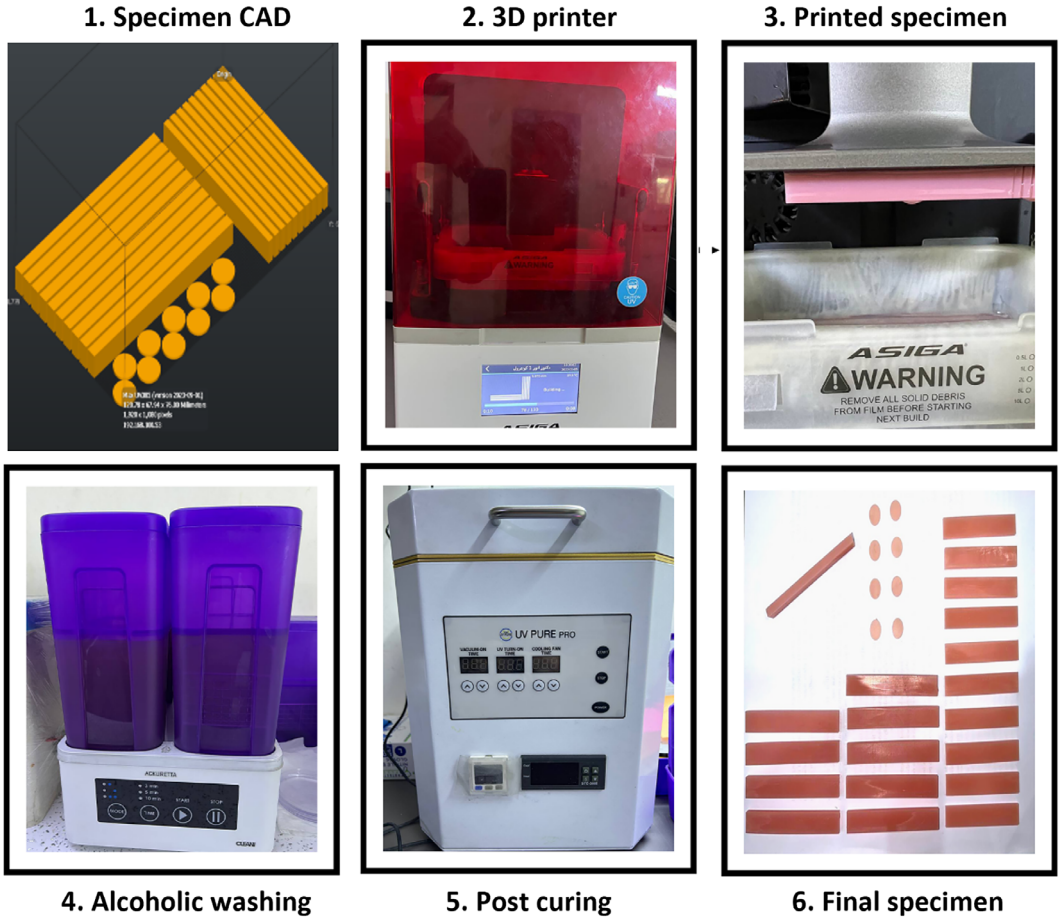

FIGURE 2 Fabrication steps of 3D printed PMMA-TiO_2 nanotube composite samples. PMMA, polymethyl methacrylate; TiO_2, titanium dioxide.

specimens underwent 2 min of washing with 99.9% isopropyl alcohol to eliminate any residual noncured resin following 3 min of ultrasonic cleaning (Clean I, Ackureta, Taiwan). The specimens were subjected to a light-curing process in a UV box from Ackureta, Taiwan, with a power of 65 watts for 50 min on each side at a wavelength of 405 nm in accordance with the manufacturer's instructions. After that, the samples were finished and polished using a lathe polishing tool and an acrylic bur, as shown in Figure 2. A digital Vernier scale with an accuracy of ±0.01 mm (Kirti NDT/India) was used to measure the sample dimensions, and the sample was stored at room temperature (37°C) for conducting the tests.

2.3 | Characterization procedures

A universal Instron testing machine (Jianqiao Testing Equipment, China) was used to perform the three-point bending test. Each specimen was positioned on the testing fixture, which consisted of two parallel supports spaced 50 mm apart. A plunger positioned centrally between the supports applied a gradual load at a cross head speed of 1.0 mm/min, deflecting it until it fractured. The load cell used during the test was 500 N, and the standard of ADA specification, No. 12, 1999, was followed for testing. The following formula was used to determine the flexural strength.[22]

$$\text{Flexural strength} = \frac{3PI}{2bd^2}\left(\frac{\text{N}}{\text{mm}^2}\right), \quad (1)$$

where b is the sample width (mm), d is the sample thickness (mm), I is the span length, and P is the peak load.

The impact energy that the specimen absorbs as it fractures was measured according to ISO 179 regulations. The Charpy unnotched impact test was carried out with impact testing equipment (Amityville, New York). The specimen was supported horizontally at both ends and struck with a two-joule capacity free-swinging pendulum. The impact strength was calculated using the following formula:

$$\text{Impact strength} = \frac{E}{B.D} \times 10^3 \left(\frac{\text{KJ}}{\text{m}^2}\right), \quad (2)$$

where B is the sample width (mm), D is the sample thickness (mm), and E is the impact energy absorbed in joules.[22]

The specimens, which measured 65 by 10 by 2.5 mm, were made in compliance with the ADA standard, No. 12 (1999). A Shore D hardness testing apparatus (Time Group Inc., China) was used to assess

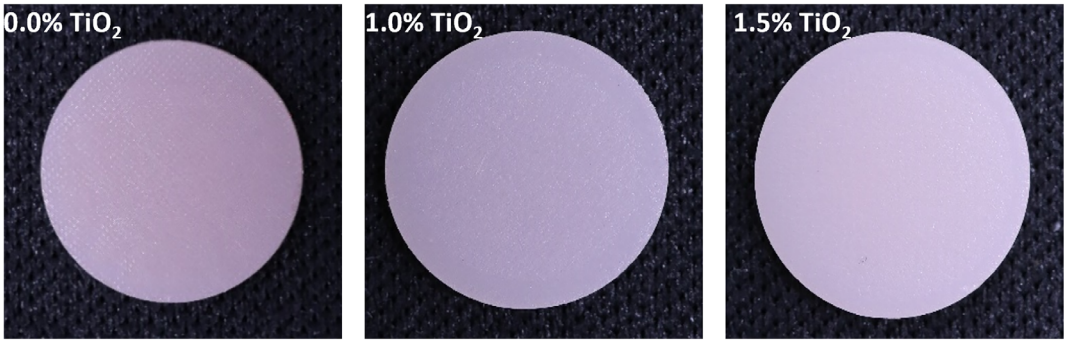

FIGURE 3 Colors of 3D printed PMMA-TiO_2 nanotube composite samples with different concentrations of TiO_2 nanotubes: 0.0 wt., 1.0 wt.%, and 1.5 wt.%. PMMA, polymethyl methacrylate; TiO_2, titanium dioxide.

the hardness of the samples. It consisted of a blunt-pointed indenter with a 0.8 mm diameter that tapered to a 1.6 mm diameter. A digital scale with a gradation of 0 to 100 units was attached to the indenter. A powerful and rapid acceleration of the indenter was applied to the samples. Direct measurements were taken using the digital scale's readout.

The surface roughness of the samples was measured with a portable digital surface profilometer (Beijing Time High Technology Ltd., China; accuracy of 0.001 μm) according to ANSI/ADA specifications (No. 12, 1999) equipped with a diamond stylus. The stylus was adjusted such that it made contact with the surface of the specimen to collect three readings from each specimen that was resting on a stiff and stable surface. The reading appears on the digital scale measured by the Ra parameter when the stylus moves 11 mm along the specimen surface. This parameter is the average of a set of single measurements of a surface's peaks and valleys. Afterwards, the mean Ra value of a sample was determined by averaging three Ra readings for each sample.

After being incubated for 24 h at 37°C, the samples were carefully cleaned with distilled water and allowed to air dry. Digital images of the control specimens and each specimen group were taken under normal room conditions using a digital imaging technique with an SLR camera (5000D Canon, Japan) and a 105 mm camera macro lens without flash on a black backdrop to discern the contrast from transparent specimens of sample.[23] With the camera in manual mode and positioned perpendicularly on a stand clamp holder 10 cm away from the specimen, all camera settings, including the shutter speed (1/60), ISO (3200), and F-stop (5.6), were fully adjusted. When shooting photos, these measurements remained the same. The digital pictures were transferred to a laptop and stored as TIFF files, as shown in Figure 3. It was clear from the images that with a higher weight percentage of TiO_2, the light pink color of the samples turned to a whiter pink color. Similar observations were also noted by other researchers.[24] These files were examined using Adobe Photoshop 2023 Version 24.5.0, a graphic design program from Adobe Systems, Inc., USA. Using built-in tools in Adobe Photoshop (Adobe Systems Inc., USA), the red, green, and blue (RGB) values were extracted via mathematical modeling and transformed into L-a-b values.[23]

Color lightness (L), hue (a), and chroma (b) were measured as part of the color study to assess each sample's color stability following the addition of TiO_2 to the basic resin used in 3D printed dentures. According to the RGB Lab system, the Adobe Photoshop graphic program was used, and the color change (ΔE) was assessed using the Commission International de l'Eclairage (CIE).[25] The sample was affixed and withdrawn at different intervals in the same orientation, running parallel to the lens of the camera equipment, while the surveyor's table remained fixed in place. According to Echlin et al.,[26] this approach ensured that the positioning was precise and constant for each measurement.

The color coordinates (L, a, and b) of each sample were measured in three different groups as follows:

I. At baseline, measurements were performed on 3D printed resin (control group) (L0, a0, b0).
II. After the addition of 1.0 wt.% TiO_2 to the resin, the color coordinates (L1, a1, b1) were measured.
III. After adding 1.0 wt.% TiO_2 to the resin, the color coordinates were measured as L2, a2, and b2.

For standardized calculation, a measurement template was created in the middle third of the samples that consisted of a square area of 60 × 60 pixels. The color data obtained directly from the color picker palette tab for the (L, a, and b) parameters where L is lightness, (0 = black; 100 = white), a is the green–red component (hue), and b is the blue–yellow component (chroma). After recording ΔL*(L0-L1, L0-L2), Δa*(a0-a1, a0-a2), and Δb*(b0-b1, b0-b2) values were calculated for each sample at each time point, and the mean values were subsequently calculated. After that, color differences (ΔE^*) were determined. The mean values are described as follows: the control group is represented by (L0, a0, b0), and the 1.0 wt.% TiO_2 experimental group is represented by (L1, a1, b1). A total of 1.5% TiO_2 (experimental group) represented by (L2, a2, b2). The total color change (ΔE^*) was calculated by Equation (3).[23]

$$\Delta E^* = \left[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\right]^{½} \quad (3)$$

Field emission scanning electron microscopy (FESEM, FEI Company, USA) was employed to examine the TiO_2 powder and fracture surface characteristics at different magnifications. The nonconductive

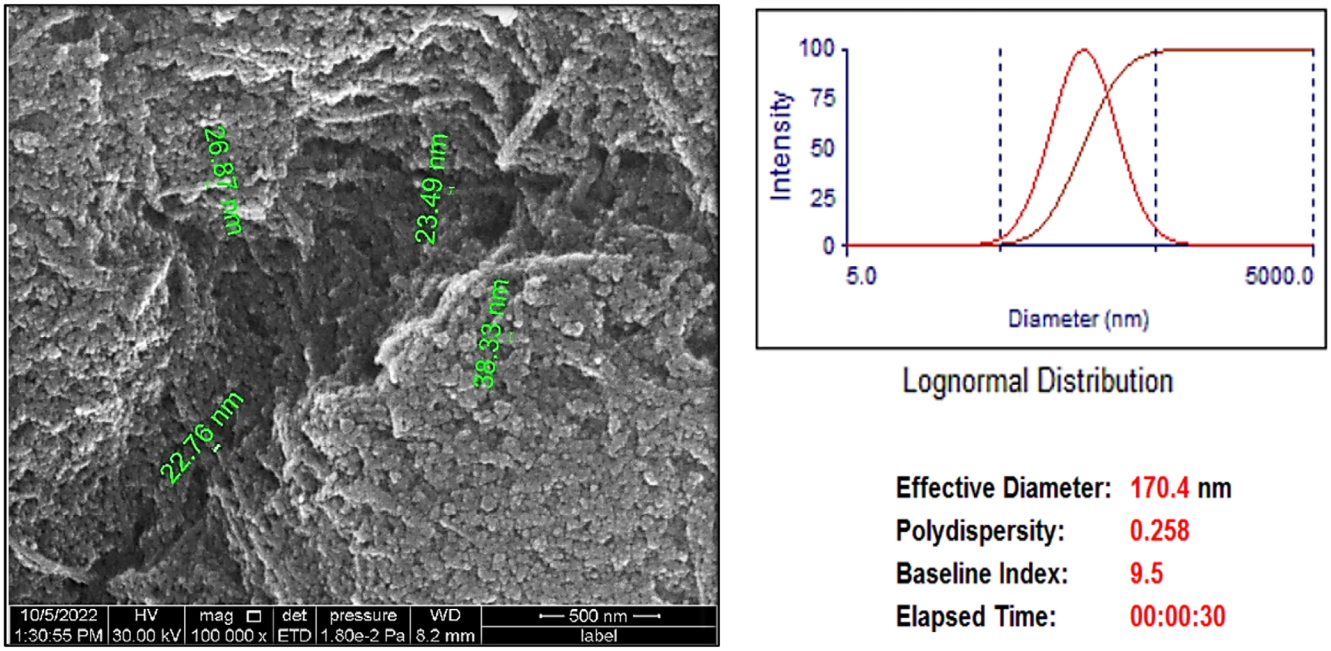

FIGURE 4 Field emission scanning electron microscopy image and particle size analysis of titanium dioxide nanotubes.

nature of the resin specimens is associated with charge build-up on the surface, leading to image distortions, blurring, or even damage to the sample. Therefore, the surfaces of the specimens are sputter-coated with an approximately 1 nm thick coating to dissipate this charge and improve the imaging quality. Energy dispersive x-ray (EDX) spectroscopy (MIRA3TESCAN, USA) was used to determine the chemical composition of the samples.[26]

2.4 | Statistical analysis

For data analysis, Prism 9 (GraphPad Software, USA) and SPSS (Statistical Package for Social Science, version 21) were utilized. For the purpose of descriptive analysis, the findings are shown as bar charts with mean values and standard deviations. One-way analysis of variance (ANOVA) and post hoc Tukey's HSD test were used. The Shapiro–Wilk test was utilized to ascertain the normality of the data distribution, while the Levene test was employed to verify the homogeneity of the data. p values greater than 0.05, less than 0.05, and less than 0.01 indicated nonsignificant, significant, and highly significant differences, respectively.

3 | RESULTS

3.1 | TiO_2 nanotube characteristics

Figure 4 shows an overall view of the TiO_2 nanotubes, revealing a large quantity of tubular materials with a narrow size distribution. The nanotubes are arranged in a random manner. It tends to congregate and attach together due to high contact surface areas. Since the material has a very porous surface, the nanotubes have a rough texture. Particle size analysis revealed that the effective particle size was 170 nm. Nanotubes take the shape of lengthy cylindrical molecules. Therefore, particle size analysis findings do not point to a specific tube dimension (diameter or length) but rather an average particle size value.

3.2 | Mechanical strength characteristics

The flexural strength (MPa) results are presented in Figure 5A and Table 1. The mean values for the 1.0% TiO_2 group were the highest (83.6 MPa). The 1.5 wt.% TiO_2 group had a mean value of 82.9 MPa, while the lowest mean value was for the control group (78.8 MPa). The flexural strength of both nanocomposite groups was significantly different from that of the control group ($p < 0.0001$). However, the difference in flexural strength between the two composite groups was not significant.

The impact strength results are presented in Figure 5B and Table 1. The mean impact strength for the 1.5 wt.% TiO_2 group was the highest (15.6 kJ/m^2), followed by that for the 1.0 wt.% group (15.5 kJ/m^2), while the lowest mean value was for found the control group (11.1 kJ/m^2). Although both composite groups were significantly different from the control group ($p < 0.000$), within themselves, the differences in terms of impact strength were not significant.

The Shore D hardness results are presented in Figure 5C and Table 1. The mean hardness of the 1.0 wt.% TiO_2 group was the highest (86.6), followed by that of the 1.5 wt.% TiO_2 group (85.0), while

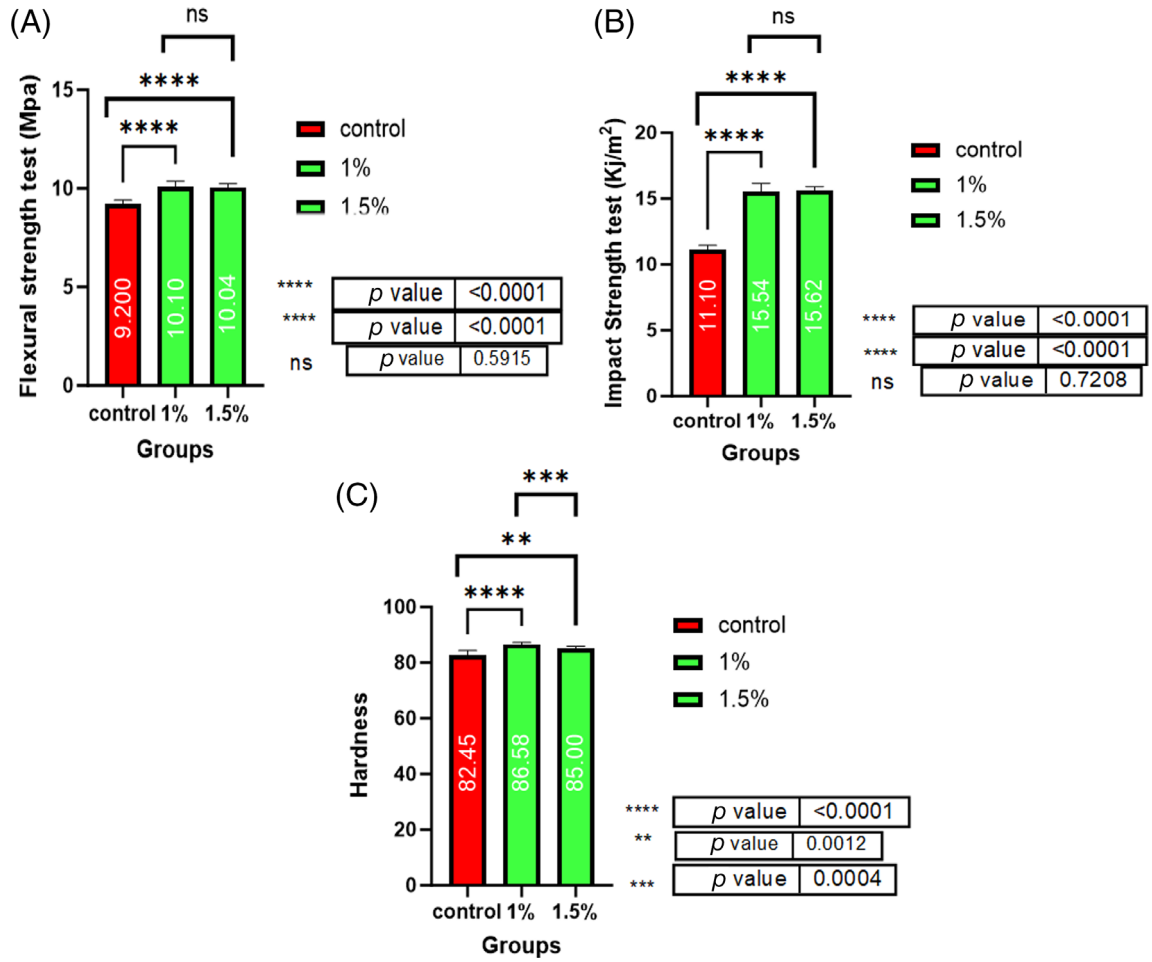

FIGURE 5 Bar graphs of mechanical characteristics of 3D printed PMMA-TiO_2 nanotube composite samples: (A) flexural strength, (B) impact strength, and (C) hardness. PMMA, polymethyl methacrylate; TiO_2, titanium dioxide.

TABLE 1 Descriptive data of the mechanical properties test results and *F* test by ANOVA.

Properties	Groups	Mean	±SD	±SE	Minimum	Maximum	*F* test	*p* value
Flexural strength MPa	Control	78.8	0.8	0.2	77.5	79.8	50.556	0.000
	1%	83.6	1.6	0.5	81.6	85.8		
	1.5%	82.9	1.4	0.4	80.8	85.0		
Impact strength KJ/m^2	Control	11.1	0.4	0.1	10.7	11.5	340.755	0.000
	1%	15.5	0.6	0.2	15.0	16.6		
	1.5%	15.6	0.3	0.1	15.3	16.1		
Shore D hardness	Control	82.5	1.8	0.6	80.7	84.7	27.085	0.000
	1%	86.6	0.7	0.2	85.7	87.8		
	1.5%	85.0	0.9	0.3	84.1	86.6		

the lowest hardness was found in the control group (82.5). The hardness values were significantly different among the groups.

3.3 | Surface and color stability characteristics

The surface roughness results are presented in Figure 6A and Table 2. The mean roughness value for the control group was 1.42 µm, followed by that for the 1.0 wt.% group (0.85 µm), while the lowest mean value was found for the 1.5 wt.% group (0.84 µm). The surface roughness values for both nanocomposite groups were significantly different from that of the control group ($p < 0.000$).

The results of the analysis of color stability are presented in Figure 6B and Table 3. The lightness parameter (value of color stability L) indicated that the 1.5 wt.% TiO_2 group had the highest mean

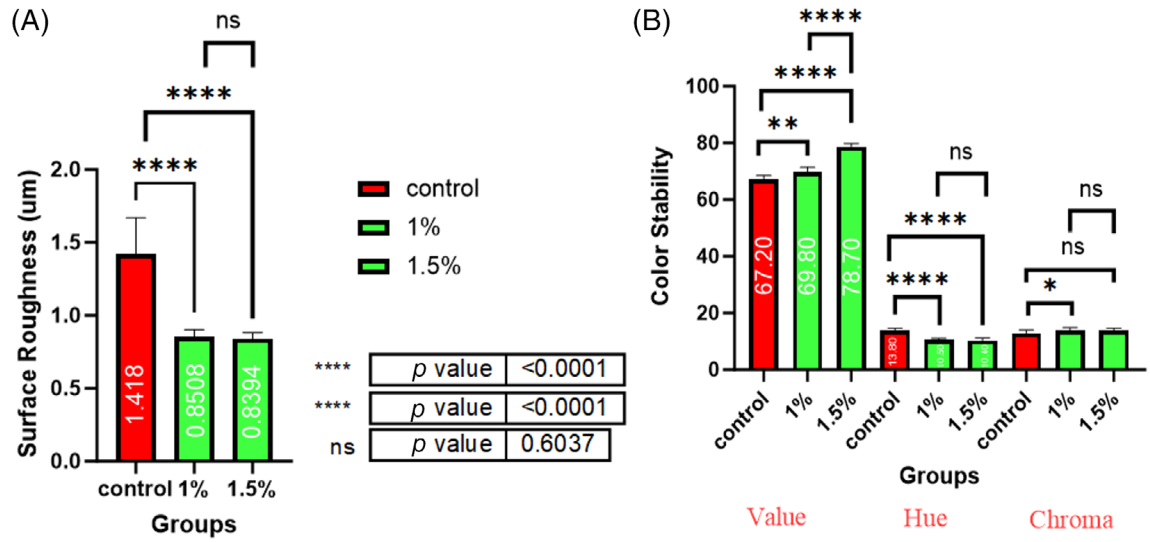

FIGURE 6 Bar graphs of physical characteristics of 3D printed PMMA-TiO_2 nanotube composite samples: (A) surface roughness and (B) color stability with three properties; value (lightness), hue (wavelength), chroma (saturation). PMMA, polymethyl methacrylate; TiO_2, titanium dioxide.

Groups	Mean (μm)	±SD	±SE	Minimum	Maximum	F test	*p* value
Control	1.42	0.25	0.08	1.07	1.70	48.406	0.000
1%	0.85	0.05	0.02	0.81	0.95		
1.5%	0.84	0.04	0.01	0.78	0.90		

TABLE 2 Descriptive data of surface roughness test results and F test by ANOVA.

TABLE 3 Descriptive data of color stability values for parameters L, a, and b and *F* test by ANOVA.

Color parameters	Groups	Mean	±SD	±SE	Minimum	Maximum	*F* test	*p* value
L	Control (L0)	67.2	1.3	0.4	65.0	69.0	184.238	0.000
	1% (L1)	69.8	1.6	0.5	68.0	72.0		
	1.5% (L2)	78.7	1.1	0.3	77.0	80.0		
a	Control (a0)	13.8	0.7	0.2	13.0	15.0	80.856	0.000
	1% (a1)	10.5	0.5	0.1	10.0	11.0		
	1.5% (a2)	10.4	0.6	0.2	9.0	11.0		
b	Control (b0)	12.8	1.1	0.3	11.0	14.0	4.145	0.027
	1% (b1)	13.9	0.8	0.2	13.0	15.0		
	1.5% (b2)	13.8	0.7	0.2	13.0	15.0		

value (78.7), followed by the 1.0 wt.% group (69.8%), while the control group had the lowest mean value (67.2%). The L values were significantly different among the groups ($p < 0.000$). On the other hand, for the hue (a) and chroma (b) parameters, the 1.5 wt.% TiO_2 group showed non-significant lower values than did the 1.0 wt.% TiO_2 group, but both nanocomposite groups showed significantly higher values than did the control group.

The total color change (ΔE^* for 1.0 wt.%) calculated between the control group and 1.0 wt.% TiO_2 group was 4.34. The total color change (ΔE^* for 1.5 wt.%) between the control group and 1.5 wt.% TiO_2 was 12.03. The results of this study showed that color instability occurred in the 3D-printed nanocomposite when the values were greater than the clinically acceptable range ($\Delta E^* < 1.5$).

3.4 | Microstructure and composition

The mechanical properties of the 3D-printed denture base resin improved due to the well-dispersed TiO_2 nanotubes, as shown by the FESEM images (Figure 7). Figure 8 presents high-magnification images of TiO_2-reinforced PMMA, which revealed a high contact area between the nanotubes and the resin.

EDX diagrams for 3D-printed denture base resin without the incorporation of TiO_2 nanotubes are shown in Figure 9. The elemental composition of the 3D-printed resin displayed oxygen (O) and carbon (C) in the EDX analysis, as shown in Table 4 and Figure 10.

EDX spectra for 3D-printed denture base resin after the incorporation of TiO_2 nanotubes are shown in Figure 11. The presence of

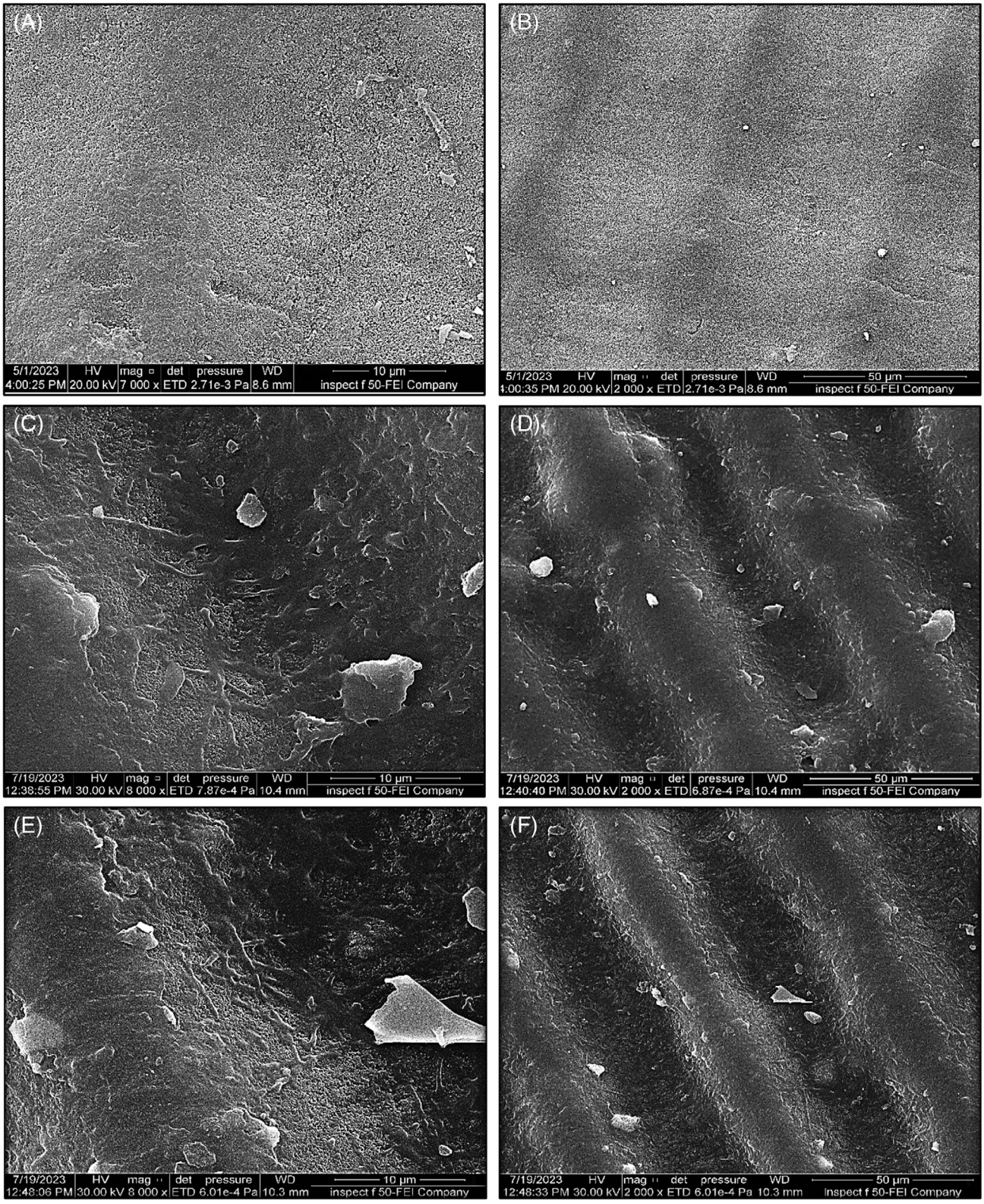

FIGURE 7 FESEM images of fractured cross sections of the samples at magnifications of ×7000 and ×2000: (A, B) control group, (C, D) 1.0% TiO_2 group, (E, F) 1.5% TiO_2 group. FESEM, field emission scanning electron microscopy; TiO_2, titanium dioxide.

titanium (Ti), oxygen (O), and carbon (C) confirmed the incorporation of TiO_2 in the 3D printed resin. The EDX analysis data shown in Table 5 indicated the presence of a higher wt.% of Ti in the 1.5 wt.% TiO_2 group than in the 1.0 wt.% group. The EDX elemental mapping in Figure 12 shows a reasonably good dispersion of Ti in the nanocomposite groups.

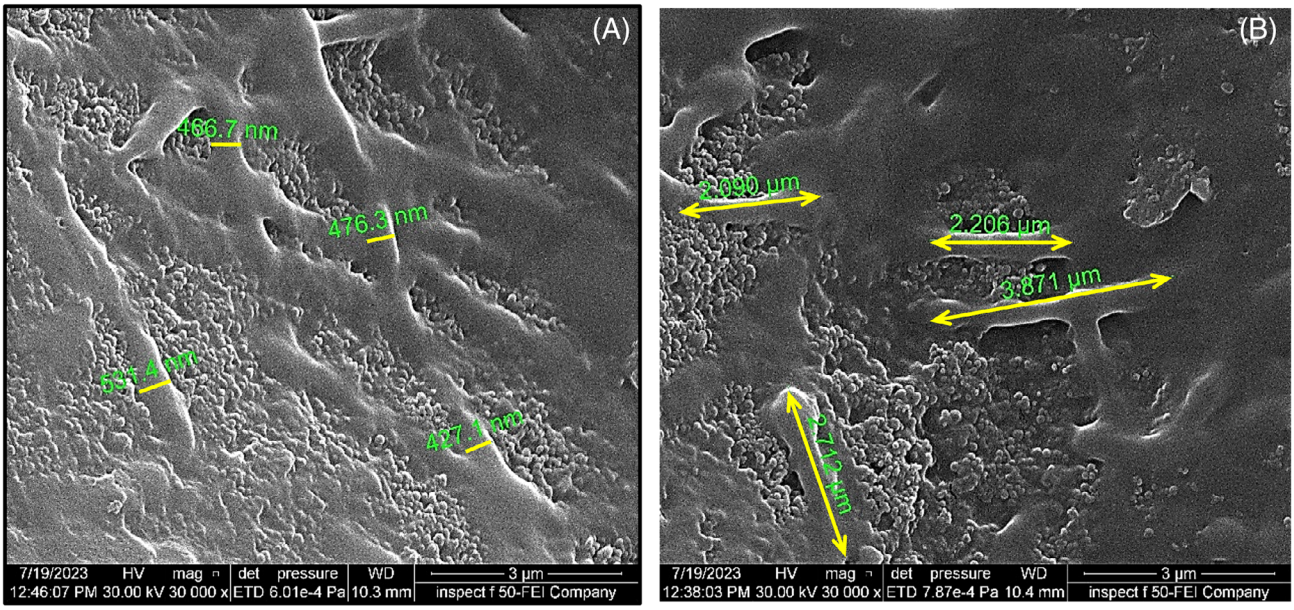

FIGURE 8 High contact areas between 3D printed TiO_2 nanotubes and PMMA resin (A) 1.5, (B) 1.0 wt.%. PMMA, polymethyl methacrylate; TiO_2, titanium dioxide.

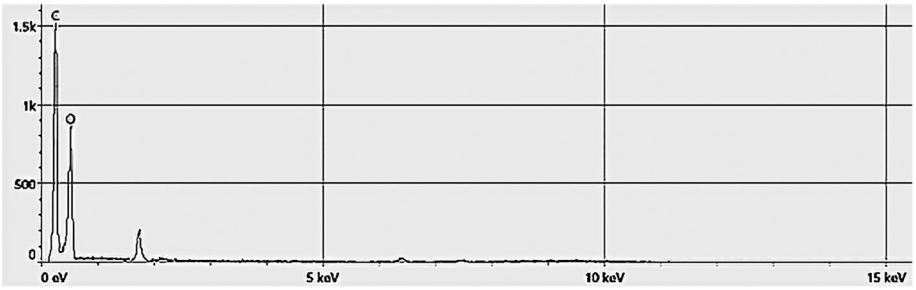

FIGURE 9 EDX diagram for 3D printed resin without incorporating TiO_2 nanotubes. EDX, energy dispersive x-ray; TiO_2, titanium oxide.

TABLE 4 Elemental analysis of 3D printed resin without incorporating TiO_2 nanotubes.

Element	Atomic %	Atomic % error	Weight %	Weight % error
C	51.9	0.6	44.8	0.5
O	48.1	0.8	55.2	1.0

4 | DISCUSSION

After adding TiO_2 nanotubes to 3D printed denture base resin, the flexural strength, impact strength, hardness, surface roughness, and color stability of the resulting material were tested. Rejecting the initial null hypothesis, the results demonstrated that the properties of the 3D-printed denture base resin were altered by the addition of TiO_2 nanotubes.

4.1 | Materials and 3D printing

3D printing was chosen for this study because of its many benefits, including its low cost and ability to produce numerous medical devices at once, without any waste of raw material or wear of rotary tools. Denture base manufacturing from liquid resin by a 3D printer is an innovative approach to denture production with better precision and repeatability and a shorter production time; nonetheless, compared to conventional denture bases, they currently exhibit poor mechanical and physical properties.

Since nanomaterials with a nanotube structure possess excellent properties that allow them to work exceptionally well in many applications, they were utilized as reinforcing materials in this study. The utilization of TiO_2 nanotubes in this study is based on their current biological applications, such as composite reinforcement, drug administration, bioscaffolds for cell culture, and titanium-based implants.[27,28] The antibacterial characteristics of the 3D printed resin were enhanced using TiO_2 NPs; however, the resulting mechanical

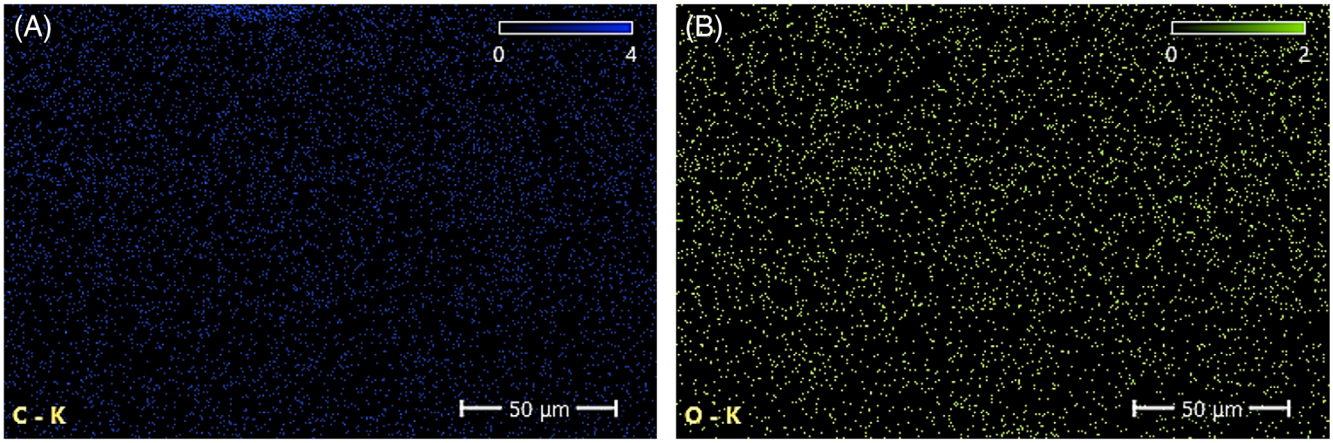

FIGURE 10 EDX mapping of the 3D printed PMMA resin only with distribution of: (A) carbon and (B) oxygen. EDX, energy dispersive x-ray; PMMA, polymethyl methacrylate.

FIGURE 11 EDX diagram of 3D printed PMMA resin after incorporating 1.0 wt.% of TiO_2 nanotubes. EDX, energy dispersive x-ray; PMMA, polymethyl methacrylate; TiO_2, titanium oxide.

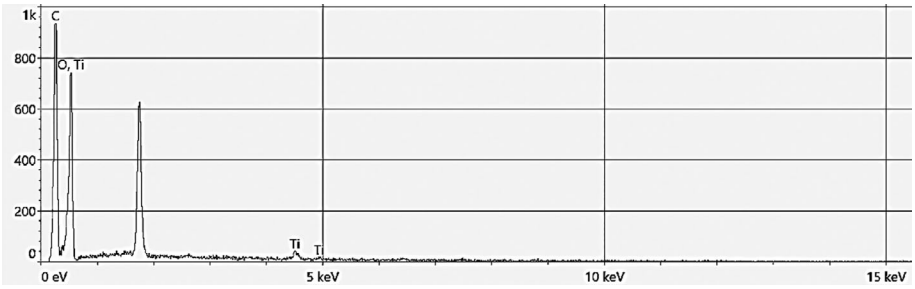

TABLE 5 EDX analysis showing the elemental composition of nanocomposite samples.

Groups	Element	Atomic %	Atomic % error	Weight %	Weight % error
1.0 wt.% TiO_2 nanotubes	C	48.4	0.7	41.1	0.6
	O	51.4	0.9	58.2	1.0
	Ti	0.2	0.0	0.7	0.1
1.5 wt.% TiO_2 nanotubes	C	48.2	0.7	41.9	0.5
	O	51.3	0.9	57.1	1.0
	Ti	0.5	0.0	1.0	0.1

Abbreviations: EDX, energy dispersive x-ray; TiO_2, titanium oxide.

properties were not tested. To determine the optimal quantity of TiO_2 nanotubes for use in this study, the printability of composite materials with different percentages of TiO_2 nanotubes was tested. Two test groups were designed to fabricate samples with 1.0 and 1.5 wt.% TiO_2 nanotubes since adding TiO_2 greater than 2.0 wt.% introduced printing failure and a declining trend in the mechanical properties, as found during the pilot study.

Because it is a faster process that generates objects with a greater resolution, the DLP printer was chosen for this study. One advantage of DLP technology over SLA is that, instead of scanning each region sequentially, all layers may be treated with a single laser exposure utilizing patterned laser light. Due to this advantage, the construction time is independent of the number of objects or the geometry of the corresponding layer.[7] The mechanical and physical properties of 3D-printed resin can be affected by a variety of factors, including the building parameters, orientation during creation, postcuring technique, program, layer thickness, layer quantity, and layer shrinkage. The printing settings are usually defined by the manufacturer, with the exception of the invariable layer thickness and printing orientation.[29] A 100 µm layer thickness is deemed sufficient for thicknesses ranging from 25 to 200 µm. The strength of a 3D-printed item increases with decreasing layer thickness due to improved resin drying and fewer dimensional changes.[30] Thinner layers also better capture geometric features, although these advantages are not without their costs and print failure risks. The study used a 50 µm layer thickness to strike a fine balance to obtain the best quality without any print failures. Asiga Composer, which has many important features, such as printing with different layer

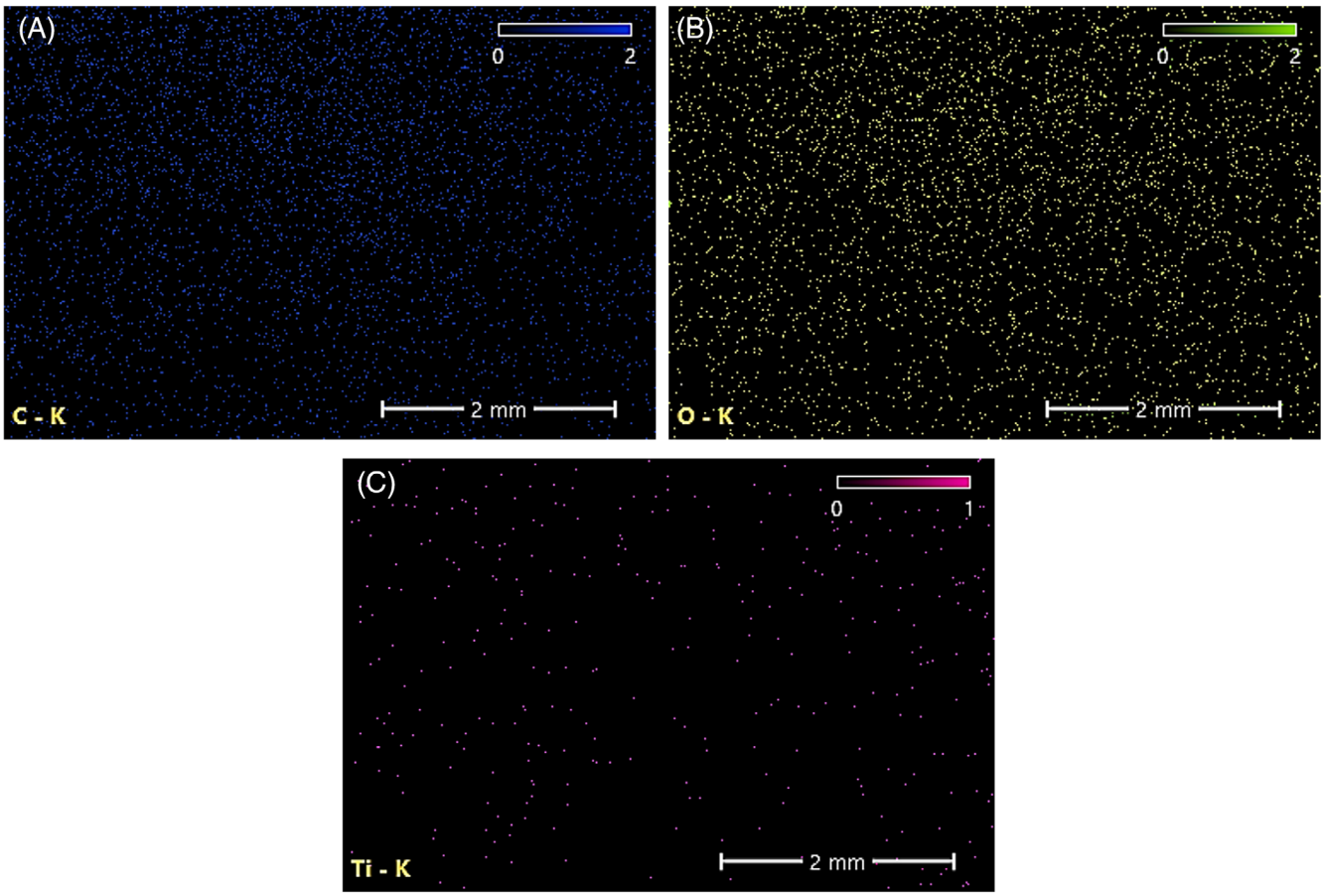

FIGURE 12 EDX mapping of the 3D printed resin incorporated with 1.0 wt.% of TiO_2 nanotubes with distribution of: (A) carbon, (B) oxygen, and (C) titanium. EDX, energy dispersive x-ray; TiO_2, titanium oxide.

thicknesses, automatic build preparation, automatic geometry repair, and unrestricted print optimization, has allowed to make appropriate adjustments.

4.2 | Mechanical properties

Flexural strength, also known as bending strength or transverse rupture strength, is a material property defined as the stress in a material just before it yields in a flexure test. Since a denture base may fracture in real life for various reasons, it is important that its material has high flexural strength.[7]

Because it directly reflects the material resistance to fracture, a high flexural strength of denture base acrylic is desired because it allows the denture to show improved clinical performance.[31] In this study, the incorporation of 1.0 and 1.5 wt.% TiO_2 nanotubes resulted in an increase in the flexural strength compared to that of the control (0% TiO_2) group, and this increase was statistically highly significant for both experimental groups. The low flexural strength of the control (0% TiO_2) could be the result of layer-by-layer printing along the specimens, lines showing how successive layers were stacked during printing are plainly evident in Figure 6, and photopolymerization of the 3D-printed resin; when printing the specimen, the air trapped in the resin might cause some voids to form inside and between the printed layers. The mechanical characteristics of the printed samples were impacted by these voids.

The interactions between the fillers and the composite matrix primarily determine the flexural characteristics of a reinforced composite. The interfacial adhesion of fillers and the matrix in a composite structure shows how interfacial shear stress is transferred from the filler to the matrix. The load transmission in the PMMA resin increased with the amount of TiO_2 nanotubes due to an increase in the contact area between the reinforced fillers and the matrix.[32] The flexural strength slightly decreased for the 1.5 wt.% group but was still significantly greater than that of the control group. These results are explained by the impact of the nanosized oxides on the internal structure of the polymerized PMMA. It has been shown that adding excessive nanofiller to acrylic resin will reduce its flexural strength because it acts as an impurity. The degree of conversion is negatively impacted by TiO_2 NPs dispersion in the PMMA matrix, which increases the amount of unreacted monomer that remains and serves as a plasticizer. In particular, the optimum concentration of nano additives is quite important to exploit their benefit in terms of improving the various properties of the denture base.[33] This finding aligns with

previous studies that examined the effects of different NPs on 3D-printed resins. For example, modifying denture-base resins with SiO_2 NPs[34] or with ZrO_2 NPs by[35] increased the flexural strength. Other studies by Mangal et al.[13] and Aati et al.[14] used nanodiamonds and ZrO_2 NPs respectively and reported the same effect.

The acrylic denture base resins should have a flexural strength of at least 65 MPa according to the ISO standard. In this study, the flexural strength of the 3D printed acrylic resin (without nanotubes) as the control was 78.8 MPa, and after adding 1.0 wt.% nanotube, the strength significantly increased to 83.6 MPa, an increase of more than 6%. It should be noted that a statistically significant improvement in strength might not always lead to a clinically significant outcome. Therefore, readers should be aware that even though this increase might be statistically significant, it is minimal and might not be clinically significant.

In this study, pure PMMA resin was used as a control group but not the most commonly used heat-cured PMMA as the purpose of this research was to examine the effect of adding nanotubes to a 3D-printed denture resin. However, there are numerous studies reported a wide range of values for flexural strength due to the differences in materials composition and manufacturing techniques. Altarazi et al.[36] found significantly higher mean flexural strengths for 3D printed NextDent (88.2 ± 1.5) and Formlabs (93.9 ± 8.3 MPa) resins compared to conventional heat-cured resin (73.5 ± 9.0 MPa). On the other hand, Chhabra et al.[37] reported significantly higher mean flexural strength (92.01 ± 12.14 MPa) for a heat-cured acrylic resin compared a 3D printed denture base resin (69.78 ± 7.54 MPa). Similarly, Prpi'c et al.[8] found that NextDent 3D printed resin showed lowest flexural strength when compared to a wide spectrum of heat-cured, CAD/CAM and injection molded materials. These findings were also supported by Gad et al.,[38] who found higher flexural strength for heat-polymerized (86.63 ± 1.0 MPa) in comparison with 3D-printed (69.15 ± 0.88 MPa) denture base materials. Therefore, in this study, the flexural strengths of the nanocomposites are comparable to that of conventional heat-cured resin and much higher than the minimum clinical requirements of 65 MPa.

The primary reason for denture fracture after a sudden fall is the low impact strength of denture base resin.[38] A sufficient impact strength of the denture base material is needed to prevent fractures in the event of a sudden drop. Most maxillary denture fractures are caused by impact and fatigue, while 80% of mandibular denture fractures are caused by impact forces.[39] Impact strength tests, conducted in either the Charpy or Izod setups, can be used to quantify the amount of energy absorbed by materials before they shatter.[40,41] In this study, the incorporation of 1.0 and 1.5 wt.% TiO_2 caused an increase in the impact strength compared to that of the control (0% TiO_2) group, and this increase was statistically highly significant for both experimental groups. On the other hand, when TiO_2 was added to the 3D-printed resin, a process of entanglement between the particle and resin occurred, which significantly increased the impact strength. This enhancement might be the result of the proper TiO_2 nanotube distribution and fine particle size, which cause a longer crack length during the fracturing process. For the PMMA reinforced with NPs employed in this study, flexible TiO_2 nanotubes that can absorb the energy of forces applied from multiple directions can be used to achieve energy absorption at the tips of fractures. The continuous, fibrous nature of the nanotubes might make it easier for the tension created in the modified denture base resin to discharge. The development of fibrils containing titanate nanotubes has also been linked to reinforced acrylic resin polymers; these fibrils may impede the spread of cracks and improve the durability of the resin structure.[42]

Good bonding between filler particles and the resin matrix can also influence crack propagation.[16] With a surface area of 250 m^2/g, the tubular form of TiO_2 is almost five times greater than that of NPs.[43] The surfaces between the wall's layers as well as its interior and exterior surfaces contribute to its large surface area.[44] The impact strength results coincide with the findings of[34] and,[13] who reported that the impact strength of 3D-printed resins increased when nanodiamond particles and SiO_2 NPs were added, respectively. Incorporating ZrO_2 NPs into 3D printed denture base resin (DentaBase, Asiga, Australia) increases the impact strength, as demonstrated in another study.[35]

Hardness is a material surface characteristic that reflects the degree of polymerization and serves as an indirect indicator of material strength through its resistance to indentation.[14] Low surface hardness denture base material may be impacted by brushing, which could result in discoloration and plaque buildup and ultimately deteriorate the integrity of the denture.[8] Resin that was printed with no titanium dioxide had a reduced hardness, which might be attributed to its composition, as well as the fact that 3D-printed resins have a lower double-bond conversion than standard denture base resins.[45] Based on the findings of this investigation, the hardness of the 3D-printed resin increased significantly with the addition of TiO_2, with an insignificant difference between the two tested TiO_2 concentrations. As previously indicated, the aligned nanotubes might contribute to the stability of the reinforced polymer. The hardness and Young's modulus of a composite reinforced with titanate nanotubes were assessed by Porras et al.[42] They concluded that the mechanical properties can be enhanced by well-dispersed nanotubes. Additionally, they proposed that longer nanotubes could result in improved mechanical properties of reinforced polymer composites in non-agglomerated nanotubes.[42] The extended length of the artificial nanotubes employed in this investigation may enhance the mechanical characteristics of modified denture base resins. Arash et al.[32] also reported on the impact of nanotube length on mechanical properties, noting that longer nanotubes had greater interfacial areas and hence superior mechanical characteristics. The increase in hardness due to the addition of 0.25 wt.% and 0.5 wt.% SiO_2 NPs to the NextDent 3D printed resin when the specimens were printed at a 90° orientation and a layer thickness of 50 μm was consistent with the findings of this study.[34] In contrast, Alshaikh et al.[35] reported that when 0.5, 1.0, 3.0, and 5.0 wt.% ZrO_2 NPs were added to NextDent and ASIGA 3D-printed resins, the hardness decreased somewhat in comparison to that of the resin that was left unaltered. Conflict may arise due to differences in the kind, concentration, and composition of the NPs

added to the resin. However, adding 5.0 wt.% ZrO_2 NPs to each resin resulted in a negligible increase in the hardness. This increase might be the consequence of the saturation of the printed specimens with high ZrO_2 NP concentrations.

4.3 | Physical properties

Determining the surface roughness involves measuring the surface texture of fine irregularities. Denture bases with rougher surfaces are prone to staining and act as an environment for microbiological adherence that causes denture stomatitis. Ra should therefore be less than or almost the lowest clinically admissible value (0.2 μm), and a denture base with a smooth surface is required.[46] 3D printing process characteristics such as layer-by-layer building of samples and printing direction could be the cause of the increased Ra. The current investigation revealed that the addition of 1.0 and 1.5 wt.% TiO_2 reduced the surface roughness compared to that of the control group and that this reduction was statistically significant across all the groups. The thinnest surface roughness observed for the 3D-printed resin may be attributed to layer thicknesses of approximately 50 μm. A smoother surface is the result of the closely packed layers, and according to Zidan et al., the inclusion of NPs would minimize micro-gaps between the resin matrix and particles, thereby reducing surface irregularities and voids that might develop on sample surfaces during denture base material processing.[47] These elements may cause the surface roughness to decrease.

A phenomenon of light or visual perception that allows one to distinguish between different colors as well as the quality of an object in relation to light reflected by the object. This is typically assessed visually by measuring the hue, saturation, and brightness of the reflected light.[48] The color change of denture base materials during extended usage can be influenced by a number of variables, including surface roughness, water absorption, stain buildup, and intrinsic pigment degradation. In regard to dental materials, color change is crucial since it establishes the material's clinical suitability for the operator. Prosthetic material color changes can cause patient discomfort and unhappiness as well as increased replacement costs.

In this study, a noncontact technique was used for measuring color via digital imaging. Using a light-sensing substance, digital cameras capture the scene and produce images with RGB values for each pixel. Non-contact measurement, the ability to reduce systematic error caused by translucency and surface curvature, the provision of a permanent database of images that can be analyzed and reinvestigated at a later time, quick and easy training, and the lack of a need for a clinician are among the benefits of this approach.[49] Another benefit of cameras is their ability to capture color information at every spatial position on the tooth, unlike other devices such as spectrophotometers, spectroradiometers, and colorimeters, which can only record spatially averaged color.[50]

The L values of color (lightness) between the control group and the 1.0% TiO_2 group demonstrated a statistically significant increase in opacity and lightness. The L values of color (lightness) between the control group and the 1.5% TiO_2 group demonstrated a further significant increase in opacity and lightness. This is supported by the data presented in Table 3 and Figure 6B. The addition of TiO_2 resulted in greater greening, as indicated by the Δa^* (hue) color change values of Δa^*(a0–a1) and Δa^*(a0–a2). However, these changes were considerably different from those in the control group in terms of the hue of the color, as shown in Table 3 and Figure 6B. The Δb^* (chroma) color change indicated an increase in the bluish hue with the addition of TiO_2. When introducing 1% TiO_2 (with a minor but noticeable difference) compared to the control group, the addition of 1.5% TiO_2 (with no significant difference) resulted in a more pronounced bluish hue in the color of the chroma, as shown in Table 3 and Figure 6B.

The total color change (ΔE^* for 1.0 wt.%) calculated between the control group and the 1.0 wt.% TiO_2 group was 4.34. The total color change (ΔE^* for 1.5 wt.%) between the control group and 1.5 wt.% TiO_2 was recorded as 12.03. Results of this study showed that color instability occurred in the 3D printed nanocomposite as the ΔE^* values were greater than 1.5, a commonly acceptable clinical limit.[51] It is known that both extrinsic and intrinsic causes can produce chromatic modification and changes in color value.[23] This can be solved by addition of appropriate extrinsic color pigment to the 3D printed nanocomposite to take advantage of the enhancement in mechanical properties due to the addition of TiO_2.

The scattering effect of nanotubes can be identified as the cause of the reduction in light transmission. Light dispersion occurs because the refraction indices of the nanotube and denture base resins differ. The material will seem brighter and have less translucency due to the scattering effect; this finding agrees with the findings in.[23] According to,[52,53] some light may be partially absorbed, and some may be partially reflected, which illustrates the consequences of the interaction of light with the nanotubes, which reduces the amount of light transmitted.

4.4 | Microstructural and compositional properties

FESEM images showed that the 1% by weight TiO_2 in the 3D-printed material was evenly distributed, with no particle clustering observed. In this study, a sonicator was used to evenly disperse TiO_2 nanotubes in alcohol. Then, the mixture was added to resin that was already on a magnetic stirrer at 60°C for 90 min. This lowered the viscosity, which improved the mixing, and it also allowed the alcohol to evaporate. When the nanotube percentage was increased to 1.5 wt.%, the TiO_2 was spread out evenly, but some evidence of agglomeration was observed. With a hollow chamber in the middle, nanotubes are long, cylinder-shaped objects. A titanate nanotube wall is always composed of layers, with between two and ten layers. The surface area-to-volume ratio of titania is enhanced by its tubular shape and multilayered structure, which also enhances its unique properties and interfacial interactions.[20] This hollow structure of the nanotubes allows interlocking with the matrix on the internal and external surfaces of the TiO_2 particles, resulting in reduced polymerization shrinkage and improved mechanical properties.[27]

4.5 | Limitations, future work, and significance

3D-printed materials offer potential as substitutes for traditional materials, a proposition reinforced by recent research. Due to the lack of previous research on the use of TiO_2 and nanotubes in 3D printed dental resin, the optimum percentages of nanotubes determined in this study could not be directly compared. However, the optimum percentage of TiO_2 nanotubes determined in this study was also close to that in another study where TiO_2 NPs were used.[54] It should be noted that only one 3D printed resin with one printing orientation and a post-printing polymerization process was used in this study. Therefore, caution should be taken in interpreting the findings, as the results could vary with the resin, printing technique and printing configuration used. According to the device's manufacturer, the surface roughness (Ra) was measured 3 times per sample (all in the same direction). It would be preferable to perform measurements in both the horizontal and vertical directions. The facts are that as it is only a 2D measurement, only one parameter (Ra) and only one direction measurements per sample might limit the overall validity of the results. A maximum variation of ±10% was found in the sample dimension measurements particularly for the thickness of the samples, which might affect the flexural and impact strength results to a certain extent. A very small percentage of TiO_2 nanotubes (less than 1.5%) was added to the denture base resin, which might cause a non-significant increase in the cost (estimated to be less than 4%) of a denture.

Even though better mechanical and physical properties are achieved in simple rectangular samples with the incorporation of TiO_2 nanotubes in denture base resin, longer time performance with functional denture base made from the nanocomposite would help in the transition toward the next step of clinical implementation. Although there was no evidence of large particle clustering or particle debonding in the high-magnification SEM images, surface modifications should be made to the TiO_2 nanotubes to promote increased interfacial bonding between the nanotubes and the denture base polymer matrix. Furthermore, assessing the mechanical or physical properties under dry conditions without significant aging in different liquid media, such as water, artificial saliva, or coffee, does not reflect the performance in real-life oral environments. Therefore, further studies will be conducted to assess the properties of the nanocomposite materials after accelerated aging in certain media. Future studies should focus on determining the optimal titanium nanotube concentration for achieving the desired biological properties of denture base resins, such as biocompatibility and antibacterial effects. It was also found that by adding PEEK (1–3 wt.%) with TiO_2 (1 wt.%), the mechanical strength of 3D printed PMMA could be improved more than by adding only TiO_2 due to a synergetic effect.[55] Therefore, hybrid 3D printed nanocomposites made by adding other NPs to TiO_2 nanotubes could be investigated for further improvement of their properties.

5 | CONCLUSIONS

Within the limitations of this study, the following conclusions can be deduced.

1. For the first time, 3D printed resin nanocomposites were successfully printed by a DLP printer at 1.0 and 1.5 wt.% concentrations of TiO_2 nanotubes.
2. The mechanical properties of the 3D printed denture base resin, such as its flexural strength and impact strength, were enhanced by the addition of TiO_2 nanotubes (1.0 and 1.5 wt.%). The main advantage was realized for the impact strength, but the improvement was minimal for the flexural strength, which might not be clinically significant.
3. The surface roughness of the denture base resin decreased, and its hardness was slightly enhanced by the addition of 1.0 and 1.5 wt.% TiO_2 nanotubes. The improvement was proportional to the concentration of the nanotubes.
4. The addition of 1.0 and 1.5 wt.% to the 3D printed resin altered the color stability.
5. The TiO_2 nanotubes were uniformly distributed inside the 3D printed resin, as evidenced by the high-magnification SEM images and EDX elemental distribution map.

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CONFLICT OF INTEREST STATEMENT

The authors do not have any financial interest in the companies whose materials are included in this article.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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