



Effects of incorporation of 2.5 and 5 wt% TiO₂ nanotubes on fracture toughness, flexural strength, and microhardness of denture base poly methyl methacrylate (PMMA)

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PURPOSE. The aim of this preliminary study was to investigate, for the first time, the effects of addition of titania nanotubes (n-TiO₂) to poly methyl methacrylate (PMMA) on mechanical properties of PMMA denture base.

MATERIALS AND METHODS. TiO₂ nanotubes were prepared using alkaline hydrothermal process. Obtained nanotubes were assessed using FESEM-EDX, XRD, and FT-IR. For 3 experiments of this study (fracture toughness, three-point bending flexural strength, and Vickers microhardness), 135 specimens were prepared according to ISO 20795-1:2013 (n of each experiment=45). For each experiment, PMMA was mixed with 0% (control), 2.5 wt%, and 5 wt% nanotubes. From each TiO₂:PMMA ratio, 15 specimens were fabricated for each experiment. Effects of n-TiO₂ addition on 3 mechanical properties were assessed using Pearson, ANOVA, and Tukey tests.

RESULTS. SEM images of n-TiO₂ exhibited the presence of elongated tubular structures. The XRD pattern of synthesized n-TiO₂ represented the anatase crystal phase of TiO₂. Moderate to very strong significant positive correlations were observed between the concentration of n-TiO₂ and each of the 3 physicomaterial properties of PMMA (Pearson's *P* value ≤.001, correlation coefficient ranging between 0.5 and 0.9). Flexural strength and hardness values of specimens modified with both 2.5 and 5 wt% n-TiO₂ were significantly higher than those of control (*P*≤.001). Fracture toughness of samples reinforced with 5 wt% n-TiO₂ (but not those of 2.5% n-TiO₂) was higher than control (*P*=.002).

CONCLUSION. Titania nanotubes were successfully introduced for the first time as a means of enhancing the hardness, flexural strength, and fracture toughness of denture base PMMA. [J Adv Prosthodont 2018;10:113-21]

KEYWORDS: Titania nanotubes; Denture base resin; Poly methyl methacrylate (PMMA); Fracture toughness; Flexural strength; Vickers microhardness

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a Equal contribution

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INTRODUCTION

Poly methyl methacrylate (PMMA) has been used as a denture base material because of its desirable characteristics such as ease of processing, chemical stability, durability, moderate cost, light weight, color matching, and stability.¹ Despite of these favorable properties, the acrylic denture base material has not fulfilled all the intended mechanical properties. Hence, there is a need for improvement of the mechanical properties of poly methyl methacrylate-based prostheses, and different methods have been introduced to improve its mechanical properties such as chemical modification by addition of rubber graft copolymers like butadiene styrene and reinforcement of poly methyl methacrylate by the addition of fibers, fillers, and materials like ultra-high modulus polyethylene.²⁻¹² Glass fiber,⁵ carbon fibers, aramid fiber, and nylon fibers^{6,7} are some of the fibers used to strengthen acrylic resins.

Incorporation of metal wires is another approach for reinforcement of PMMA.^{8,9} Poor adhesion between the resin matrix and the wire is a problem with this technique. Therefore, metallic fillers have been considered by different researchers for the improvement of physical and mechanical properties of acrylic resins. Sehajpal and Sood¹¹ evaluated the effect of the addition of various amounts of powdered silver, copper, and aluminum on some physical properties of PMMA. They concluded that metal fillers can increase thermal conductivity and compressive strength of poly methyl methacrylate.¹⁰ Asar *et al.*¹² added various amounts of metal oxides including Al₂O₃, TiO₂, and ZrO₂ to heat-cured acrylic resin and found that modification of acrylic resin with certain amounts of metal oxides led to a significant increase in mechanical properties and a decrease in water sorption and solubility. They concluded that metal oxides may be useful to prevent denture fractures resulting from fluids of the oral environment.¹²

The introduction of nano-scale materials offers new aspects for improvement of the mechanical properties of polymers. Interest in nanostructures has been driven by their high surface area to volume ratio, which increases the interfacial interaction and the specific characteristics of them including new biological, physical, and chemical properties.¹³ Recently nanotubes have been considered for reinforcement of PMMA denture base resins. Carbon nanotubes,^{14,15} zirconia nanotubes,¹⁶ titania nanotubes, and halloysite nanotubes¹⁷ are some nanotubes which are employed for reinforcement of denture base resins. Wang *et al.*¹⁵ reinforced poly methyl methacrylate denture base material using 0.5 wt%, 1 wt%, and 2 wt% of Multiwalled carbon nanotubes. Their results indicated improved flexural strength by addition of 0.5% and 1% MWCNTs but not for the 2% MWCNTs reinforced group due to the poor dispersion of CNTs fillers throughout the matrix. Yu *et al.*¹⁶ modified denture base PMMA with ZrO₂ nanotubes and ZrO₂ nanoparticles and concluded that ZrO₂ nanotubes had a better reinforcement effect than ZrO₂ nanoparticles. Abdallah¹⁷ evaluated the mechanical properties of PMMA resin reinforced

with halloysite nanotubes and stated that addition of low percentages of HNTs into resin matrix increases the hardness values significantly, but the flexural strength and Young's modulus did not improve significantly.

TiO₂ particles have been used as filler added to PMMA because of their effect on the mechanical properties of acrylic resins^{18,19} and their antibacterial properties.^{20,21} Furthermore, TiO₂ particles are preferred in dentistry due to their desirable color and excellent biocompatibility, as well as durability.²² In 1998, investigators discovered a tubular shape for hydrothermally synthesized titanium oxide nanostructures.^{23,24} Such linear nanotubes can exhibit increased surface area compared with nanoparticles.²⁵ Among the various nanotubes, the TiO₂ nanotube (TNT, n-TiO₂) has been considered due to its high-specific surface area, photocatalytic property, and ion-exchangeability.²⁶ The tubular form of titania has a surface area of 250 m²/g, which is about five times that of the nanoparticle.²⁷ The high surface area results from the internal and external surfaces and the surfaces between the layers of the walls.²³ Recently, titania nanotubes have been used for biological applications including drug delivery, bio-scaffolds for cell cultures, titanium-based implants and reinforcement of composites.²⁸⁻³¹ Michele *et al.*²⁸ reported increased Young's modulus and strength of reinforced polystyrene with functionalized titania nanotubes. Porras *et al.*²⁹ also found improved mechanical properties of poly (ethylene oxide)/chitosan polymer composite modified with hydrothermal synthesized titanate nanotubes. Enhancement of mechanical properties of resin based cement reinforced with titania nanotubes was also reported by Khaled *et al.*³² In another study, Dafar *et al.*³¹ investigated the mechanical properties of flowable dental composites reinforced with titanium dioxide nanotubes and discovered improvement in fracture toughness and Young's modulus in the experimented composite.

To the best of our knowledge, the literature lacks any studies that used TiO₂ nanotubes to reinforce denture base polymers, although few studies have employed TiO₂ nanoparticles as added fillers to enhance mechanical properties of PMMA-based prostheses and have reported controversial results.^{19,33,34} Since no previous study has evaluated the addition of titanium oxide nanotubes to PMMA denture base, this preliminary multi-phase study was conducted. It aimed to prepare titania nanotubes, evaluate their properties, and assess the reinforcement potential of hydrothermally synthesized titanium oxide nanotubes added to a commercial PMMA denture base on microhardness, fracture toughness, and flexural strength of resin.

The null hypothesis of this study was lack of effect of addition of Titanium Dioxide Nanotubes on mechanical properties of the acrylic resin denture base material.

MATERIALS AND METHODS

TiO₂ nanotubes were prepared using an alkaline hydrothermal process.³⁵ The precursor was a commercial TiO₂ powder (SkySpring Nanomaterials Inc., Houston, TX, USA) with a crystalline structure of ca.99.5% anatase and particle

size of 10 - 30 nm. The procedure of nanotube synthesizing was started by treating 1.14 g of nanoparticle powder with 40 - 45 mL of 10 N NaOH solution. Afterwards, the suspension was sealed in a Teflon-lined autoclave at 150°C for 48 hours. Subsequent to the heating process, the resultant precipitates were washed with deionized water and HCl aqueous solution (1 M) until the pH of the solution became about 7. Finally, an oven was used to dry the powders at 80°C for 3 hours to synthesize nanotubes.

The crystalline phase of the synthesized titania nanotubes was investigated by powder X-ray diffraction (XRD, INEL, Equinox 3000) using Cu K α radiation (40 kV, 30 mA). Data were compiled at a scattering angle of 2 θ from 2° to 80° at a step size of 0.032° and 1°/s scan speed.

Fourier transform infrared spectroscopy (FTIR, Nicolet iS50, Madison, WI, USA) using the KBr pellet method was used to assess the n-TiO₂ tubes by adding 0.2 g anhydrous KBr to 2 mg of titania nanotubes. Information was obtained at a resolution of 4 cm⁻¹ and wavenumbers ranging between 400 and 4000 cm⁻¹.

The morphology and elemental analysis of n-TiO₂ was performed using a field emission scanning electron microscope (FESEM, ZEISS Co., Germany) at an accelerating voltage of 15 kV equipped with an energy dispersive X-ray (EDX) spectrometer (AURIGA, ZEISS).

In order to perform fracture toughness (K_{IC}), flexural strength, and Vickers microhardness tests, 45 PMMA specimens were fabricated for each phase: the specimens in each project were assigned to three groups (n = 15) according to the percentage of titania nanotubes including TNT 0% (control), TNT 2.5% and TNT 5% by weight. Therefore, 135 specimens (45 specimens for each sub-project) were prepared according to ISO 20795-1:2013 standard and instructions of the manufacturer.³⁶ The size and shape of the specimens differed for each of the 3 sub-projects (they were bar-shaped with 2 sizes for flexural strength and toughness tests, while they were discoid for microhardness tests, detailed below). Wax templates were used to shape the

specimens during their heating / fabrication procedure (Fig. 1). There were 3 groups: specimens made of PMMA only (control, n = 45), those made of PMMA + 2.5 wt% TNT (n = 45), and those made of PMMA + 5 wt% TNT (n = 45). To create the experimental groups, the powder of conventional acrylic resin was blended with 2.5 wt% and 5 wt% of synthesized titanium dioxide nanotubes as follows. The TiO₂ nanotubes and the powder of a conventional denture base resin (mega CRYL HOT, megadental GmbH, Bidingen, Germany) weighted in an analytical balance (Sartorius, Goettingen, Germany) precisely and divided into equal parts. Then each part of n-TiO₂ powder was mixed manually with powder of acrylic resin for 3 minutes, subsequently they mixed with an amalgamator device (Ultramat 2, SDI, Australia) to obtain an adequate particle distribution.

2.3 gr of modified and unmodified powder with 1 mL liquid (monomer) of denture base resin was mixed according the manufacturer's instructions and packed in a dough stage in the dental stone molds (Hydrocal dental stone, Moldano, Bayer Lerekusen, Germany). The two portions of the flask were closed tightly together and placed under the hydraulic press at 40,000 N, and the pressure was slowly applied on the flask so that the dough evenly flowed throughout the mold space. The pressure was then released, the flask was opened, and the excess material was removed with a sharp scalpel. A second trail closure also was performed. Finally, the two portions of the flask were closed and left under pressure (20 bars) for 5 minutes. Subsequently the flask was clamped and maintained under low pressure for 30 minutes, and then transferred to a water bath at room temperature. The temperature was slowly elevated to 73 ± 1°C for 90 minutes and then raised to the boiling point at 100°C for 30 minutes. Before opening, the flasks were subjected to bench cooling. All specimens were finished and polished to obtain a smooth and glossy surface.

Before testing the flexural strength and fracture toughness, the specimens were incubated by water storage at 37°C according to the ISO standard. The durations of water storage were 48 hours and 120 hours for flexural strength and fracture toughness tests, respectively. No water storage was done before Vickers microhardness test.

Bar-shaped specimens with dimensions of 64 × 10 × 3.5 mm³ as stated in ISO 20795-1³⁶ were fabricated. There were 45 specimens: 15 controls, 15 PMMA + 2.5 wt% TNT, and 15 PMMA + 5 wt% TNT.

After 2 days of water storage, the specimens were subjected to a three-point bending flexural strength test using a universal testing machine with a 50.0-kg load cell (Bongshin, Bongshin Loadcell Co., Ltd., Seoul, Korea) at a crosshead speed of 5 mm/min. The supporting wedges were placed 50 mm apart from each other, and the specimens centrally located on the device in a way that the loading wedge was applied on the center of the specimens. The flexural strength was calculated in mega Pascal (MPa) from the following formula: $S = 3FL/2bd^2$ where S = flexural strength, F = load at fracture (in N), L = distance between supports (in mm), b = width and d = thickness of sample (in mm).



Fig. 1. Arrangement of wax patterns within the flask.

A total of 45 bar-shaped specimens with dimensions determined according to ISO 20795-1:2013³⁶ (length 39 mm, height 8 mm, and width 4 mm) were prepared. There were 45 specimens: 15 controls, 15 PMMA + 2.5 wt% TNT, and 15 PMMA + 5 wt% TNT.

An initial notch with a depth of 3-mm was then cut along the centerline of the specimens, using a 0.5-mm thick diamond blade. Subsequently, another notch of almost 400 μm depth was cut in the middle part of the initial notch. The depth of this notch was checked using a stereomicroscope (EZ4D; Leica Microsystems Ltd., Singapore).

After 5 days of water storage, the specimens were loaded in a 3-point bending configuration (i.e., single edge-notched bend test (SENB)) using a universal testing machine with a 50.0-kg load cell (Bongshin, Bongshin Loadcell Co., Ltd., Seoul, Korea). The crosshead speed of the loading plunger was 1 mm/min and the specimen test span was 32 mm. Eventually, the critical stress intensity factor (K_{IC}) was calculated from the obtained values, as following equation:³⁶

$$K_{max} = \frac{fP_{max} l_t}{b_l b_r^{3/2}} \times \sqrt{10^{-3}} \text{ MPam}^{1/2}$$

where P_{max} is the peak load at fracture (in N), l_t is length (in mm), b_l is width (in mm), b_r is height (in mm), and f is geometrical function, which is calculated as follows:

$$f(x) = \frac{3x^{1/2}[1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)]}{2(1+2x)(1-x)^{3/2}}$$

and $x = a / b_l$

Fifteen acrylic discs (10 mm in diameter and 5 mm high) from each of the aforementioned 3 material compositions were prepared and hand-polished using silicon carbide papers up to 2000 grit to produce a glossy flat surface. After polishing, the surface microhardness (SMH) of the specimens were measured using a microhardness tester (V-Test II, Baresiss, Germany) with a Vickers diamond indenter (0.8 mm in diameter), which was attached to a digital scale from 0 to 100 units under a load of 50 g force for 10 s.^{37,38} Three measurements of Vickers pyramid numbers (HV) in each specimen were recorded at different sites along with the diametrical line. Ultimately, the average of three readings was calculated as the main finding.

After the confirmation of the normality by the Kolmogorov-Smirnov test, the data were analyzed using one-way analysis of variance (ANOVA), followed by a post-hoc Tukey's test. The correlations between the concentrations of TiO₂ nanotubes with each of the 3 physicomaterial properties of PMMA resin were evaluated using a Pearson correlation coefficient. The significance level was set at 5%. The statistical analyses were performed using SPSS 23.0 (IBM, Armonk, NY, USA).

RESULTS

The morphology of n-TiO₂ was examined by FESEM after calcination. FESEM images of n-TiO₂ exhibited the pres-

ence of elongated tubular structures with outer diameters of 11.85 nm (Fig. 2A, Fig. 2B). On the basis of the analyses using EDX, Ti (46.51 wt%) and O (52.00 wt%) were the predominant elements with the most abundance among other elements in synthesized powder (Fig. 2C). A low percentage of chloride (1.12 wt%) and trace amount of Na (0.37 wt%) were also detected.

According to International Center for Diffraction Data (ICDD PDF No. 89-4921), a sharp diffraction peak at 24.56° in addition to other peaks at 37.61°, 43.43°, 46.76° and 53.7° and 64.76° (Fig. 3) represent the anatase crystal phase of TiO₂.^{31,39}

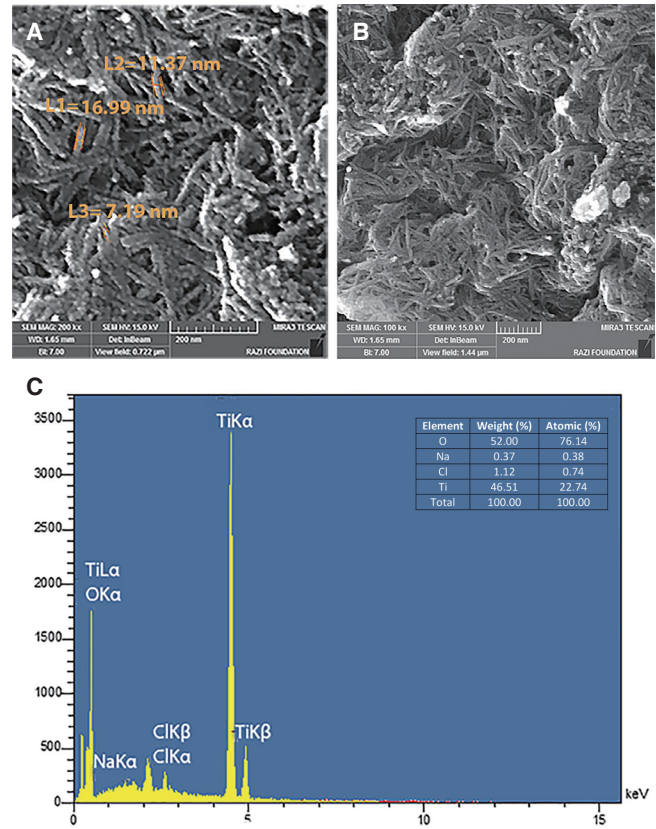


Fig. 2. (A, B) SEM image of synthesized n-TiO₂ indicates elongated tubular structures; (C) the EDS of synthesized powder in a selected region.

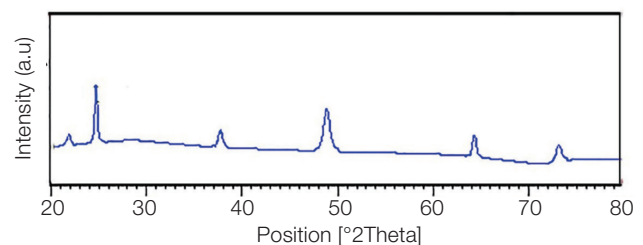


Fig. 3. X-ray diffraction of n-TiO₂ tubes.

The FTIR spectra of n-TiO₂ tubes in Fig. 4 exhibit a broad peak at 3362 cm⁻¹ which is attributed to O-H bonds associated with hydroxyl groups, and the peak at 474 cm⁻¹ is related to the O-Ti-O bonding of the anatase phase of titania.^{40,41} The sharp peak at 1672 cm⁻¹ is due to the presence of oxygen-containing groups, i.e., C-O, COO, and C=O and hydroxyl groups.^{41,42}

Mechanical properties of reinforced / control PMMA specimens are presented in Table 1 and Fig. 5. The Pearson coefficient indicated moderate to very strong positive associations between the concentration of TNT with PMMA's flexural strength ($r = 0.750$, $P < .001$), microhardness ($r = 0.894$, $P < .001$), and fracture toughness ($r = 0.501$, $P = .001$). ANOVA showed significant differences among the three material compositions (PMMA only vs 2.5% or 5% TNT), regarding their fracture toughness ($p = .003$), flexural strength ($P < .001$), and microhardness ($P < .001$, Table 1, Fig. 5). All Tukey pairwise comparisons among three flexur-

al strength groups were significant ($P < .05$). All pairwise comparisons among three Vickers hardness groups were significant as well ($P < .001$). When comparing three fracture toughness averages, only the comparison of the groups "control vs. 5 wt%" became significant ($P = .002$) and the other two comparisons were not significant ($P > 0.1$).

The values for flexural strength (FS) indicated that the acrylic resin reinforced with 5 wt% n-TiO₂ tubes exhibited the highest values for FS. The obtained flexural strength values of both 2.5 and 5 wt% groups were significantly higher than those exhibited by the un-modified group ($P < .001$). The FS values of 5 wt% were also superior to those modified with 2.5 wt% n-TiO₂ tubes ($P = .047$, Fig. 5, Table 1).

The addition of n-TiO₂ significantly influenced the surface hardness of PMMA; the obtained mean Vickers hardness values of both 2.5 and 5 wt% modified groups were significantly higher than the control group's ($P < 0.001$).

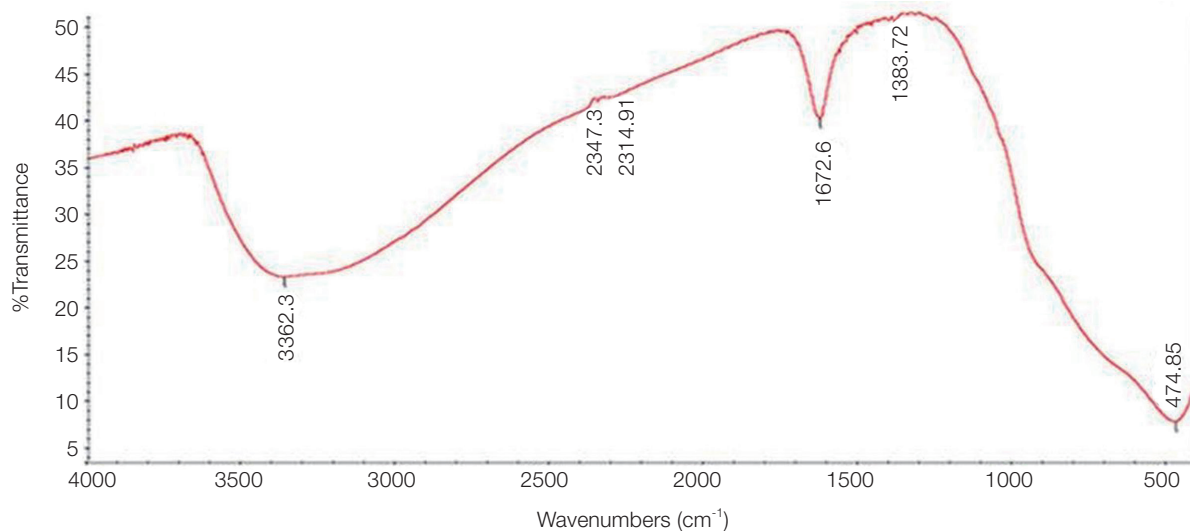


Fig. 4. FTIR spectra of n-TiO₂ tubes.

Table 1. Mechanical properties of control and reinforced PMMA with n-TiO₂ tubes

Test (unit)	TiO ₂	Mean	SD	95% CI	Min	Max	
Flexural strength (MPa)	0%	51.19	8.16	46.67	55.71	38.75	65.95
	2.5%	77.61	13.07	70.38	84.85	50.44	99.41
	5.0%	90.71	19.82	79.26	102.15	57.30	122.52
Hardness (HV)	0%	20.29	1.30	19.57	21.01	17.6	22.8
	2.5%	23.69	1.10	23.08	24.30	21.4	25.4
	5.0%	26.05	1.18	25.39	26.70	24.0	28.4
Fracture toughness (K_{IC}) (MPa m ^{1/2})	0%	2.41	0.29	2.24	2.58	2.03	3.01
	2.5%	2.75	0.41	2.53	2.98	2.18	3.44
	5.0%	3.13	0.75	2.70	3.57	2.34	4.61

SD, standard deviation; CI, confidence interval; Min, minimum; Max, maximum.

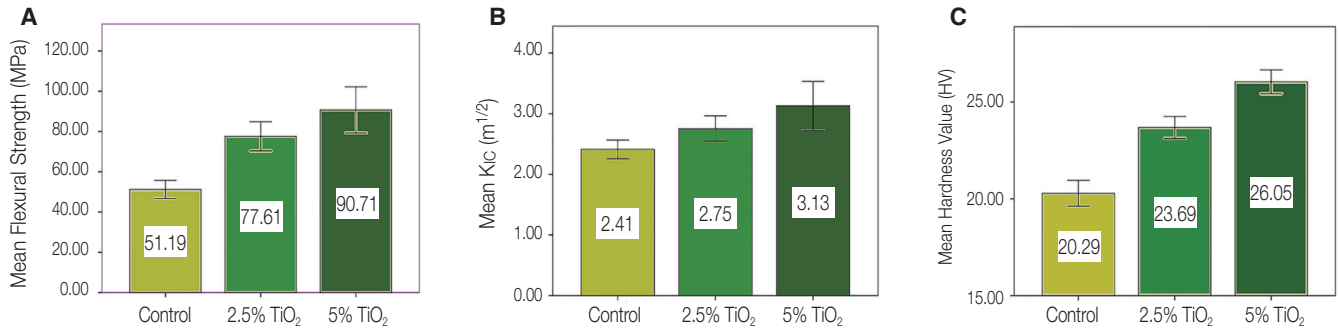


Fig. 5. (A) Mechanical properties of non-modified PPMA, (B) mechanical properties of PPMA modified with 2.5 wt% n-TiO₂ tubes, (C) mechanical properties of PPMA modified with 5 wt% n-TiO₂ tubes.

Moreover, the statistical analysis showed significant differences between the hardness values of 2.5 and 5 wt% modified groups ($P < .001$, Fig. 5, Table 1).

The fracture toughness (K_{IC}) values showed that the acrylic resin reinforced with 5 wt% n-TiO₂ tubes exhibited significantly higher K_{IC} values compared to the control group ($P = .002$). However, the K_{IC} values of specimens reinforced with 2.5 wt% were not significantly higher than those of the control group; they were also not significantly lower than the 5 wt% modified one ($P > .05$, Fig. 5, Table 1).

DISCUSSION

In the present study, denture base resins were modified with 2.5% and 5% by weight of synthesized titania nanotubes, and the mechanical properties of the modified and control groups were measured for critical stress intensity factor (K_{IC}), flexural strength, and surface microhardness. Based on the results, the null hypothesis of this study (i.e., lack of effect of the addition of TiO₂ nanotubes on mechanical properties of denture acrylic resin base) was rejected.

SEM was used to observe the morphology of synthesized nanotubes. The obtained SEM images in the current study obviously showed the tubular shapes of synthesized titanate nanotubes. It is claimed that after treating with NaOH, some Ti-O-Ti bonds break down and form the titanate sheets. Under autoclaving and high concentration of NaOH, the produced sheets exfoliate into nanosheets, and then they can scroll or fold into a tubular morphology.²³ Different studies have used driving forces for folding these nanosheets.^{23,43} It is likely that the inequality in the width of different layers of multi-walled nanosheets creates a tendency for layers to move within the walls in order to reduce the excess surface energy. Nanotubes are long cylinders with a hollow cavity in the center. The walls of titanate nanotubes are always multilayered and the number of their layers varies from 2 to 10.²³ The tubular form and multilayered structure of titania increase its surface area-to-volume ratio, which

improves the interfacial interaction and their specific characteristics. In the current study, TiO₂ nanotubes were synthesized using an alkaline hydrothermal process. This method was first reported by Kasuga *et al.*²⁴ as a simple method for preparation of TiO₂ nanotubes.

Some studies evaluated the strength of denture base resins using impact tests, which are influenced by the geometry of specimens and loading conditions and therefore may not be the best test for predicting the clinical function of the material.⁴⁴ Fracture toughness (FT) is considered one of the most important tests for the assessment of mechanical properties of dental polymers.^{45,46} FT determines the maximum energy a material can absorb through crack propagation prior to its failure; it is described by a critical intensity factor (K_{IC}), and processes that can absorb energy at the tip of a crack might improve fracture toughness.^{47,48} FT provides information about crack propagation, which is the main reason of fracture in brittle materials.^{47,48} Various test methods were introduced for the measurement of this property. In this study, we used single-edge-notched (SEN) test as described in ISO³⁶ for assessment of fracture toughness because of its validity, reliability, and simplicity of specimen preparation.^{44,46,49} In the current study, the specimens reinforced with both 2.5 and 5 wt% titanium nanotubes exhibited greater K_{IC} values than the control group, although only the difference between K_{IC} values of the 5 wt% modified group and the control was statistically significant. For the PMMA reinforced with nanotubes used in this study, absorption of energy at the tip of cracks can be achieved by flexible TNTs, which can absorb energy of forces applied from different directions. The continuous fibrous-like structure of these nanotubes may facilitate the release of the stresses produced in modified denture base resin and enhance FT. Improvement of the fracture toughness property of reinforced acrylic resin polymers can also be associated with the formation of fibrils containing titanium nanotubes, which may hinder crack propagation and increase the stability of the resin structure.²⁹ Pei Feng *et al.*⁵⁰ described that when the tip of a crack encounters TiO₂

nanotubes, the crack mainly propagates around the nanotubes; this results in additional absorption of fracture energy and improvement of fracture toughness.⁵⁰ Khaled *et al.*³² determined the use of the fiber 'pull out' phenomenon as the main reason for increased K_{IC} of PMMA-based cements reinforced with TiO₂-SrO nanotubes. They reported that this addition reduces the sites of local stress concentration, hence increasing the K_{IC} of the composite.³²

The Vickers microhardness measurements obtained in this study in both reinforced groups were significantly higher than that of the control group. As mentioned earlier, the aligned nanotubes may help maintain the stability of reinforced polymer. Porras *et al.*²⁹ evaluated the hardness and Young's modulus of a composite reinforced with titanate nanotubes. They concluded that well-dispersed nanotubes can improve mechanical properties. They also suggested that in non-agglomerated nanotubes, better mechanical properties of reinforced polymer composites can be achieved with longer nanotubes.²⁹ The high length of synthesized nanotubes used in this study might improve mechanical properties of modified denture base resins. The effect of the length of nanotubes on the mechanical properties was also reported by Arash *et al.*,⁵¹ who observed better mechanical characteristics with nanotubes having higher interfacial regions.

Flexural characteristics of a reinforced composite are affected mostly by interactions between the added fillers and matrix of the composite. In a composite structure, the interfacial adhesion of fillers and matrix indicates how interfacial shear stress transfers from the filler to the matrix.⁵² The high contact area between reinforced fillers and PMMA resin in acrylates modified with titanium nanotubes increases the load transfer.⁵² Moreover, the tubular, open-ended structure of nanotubes might cause the methyl methacrylate monomer to pass in nanotubes via capillary action and polymerize there.³² This might increase mechanical interlocking by the engagement of polymers with the internal surface of tubes. Hence, incorporated tubes and polymer molecules might create an improved matrix with a greater extent of cross-linking, leading to increased load transfer within the composites.³² This might justify the superior FS values of nanotube-reinforced acrylic resins.³²

This pilot study was limited by some factors. Since there was no previous study in this regard, selecting the percentages of nanotubes and their properties were not optimized. Therefore, due to difficulties in production of titania nanotubes, we were limited to evaluate only the effect of 0%, 2.5%, and 5% concentrations of TiO₂ nanotubes on mechanical properties of denture base resins. Further studies are needed to improve TNT's dispersion throughout the polymer matrix. To promote better interfacial interactions between denture base polymer matrix and titania nanotubes, surface modification of titanium oxide nanotubes is suggested. Future studies should be conducted to identify the optimum concentration of titania nanotubes for reaching various physicochemical and biological properties (e.g., antibacterial effects and biocompatibility) of denture base resins.

CONCLUSION

The PMMA denture base resin was successfully reinforced with hydrothermally synthesized n-TiO₂ tubes. The fracture toughness, flexural strength, and microhardness of acrylic resin were improved with the addition of nanotubes. These improvements were a linear function of the concentration of added titania nanotubes, and this phenomenon was more vivid in terms of microhardness, followed by flexural strength. Thus, this preliminary study demonstrated for the first time a promising new agent for reinforcing denture base resin materials.

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REFERENCES

1. Peyton FA. History of resins in dentistry. *Dent Clin North Am* 1975;19:211-22.
2. Johnston EP, Nicholls JI, Smith DE. Flexure fatigue of 10 commonly used denture base resins. *J Prosthet Dent* 1981;46:478-83.
3. Jagger DC, Harrison A, Jandt KD. The reinforcement of dentures. *J Oral Rehabil* 1999;26:185-94.
4. Karacaer O, Dogan OM, Tinçer T, Dogan A. Reinforcement of maxillary dentures with silane-treated ultra high modulus polyethylene fibers. *J Oral Sci* 2001;43:103-7.
5. Kim SH, Watts DC. The effect of reinforcement with woven E-glass fibers on the impact strength of complete dentures fabricated with high-impact acrylic resin. *J Prosthet Dent* 2004;91:274-80.
6. Vallittu PK. Glass fiber reinforcement in repaired acrylic resin removable dentures: preliminary results of a clinical study. *Quintessence Int* 1997;28:39-44.
7. Vojdani M, Giti R. Polyamide as a denture base material: A literature review. *J Dent (Shiraz)* 2015;16:1-9.
8. John J, Gangadhar SA, Shah I. Flexural strength of heat-polymerized polymethyl methacrylate denture resin reinforced with glass, aramid, or nylon fibers. *J Prosthet Dent* 2001;86:424-7.
9. Ruffino AR. Effect of steel strengtheners on fracture resistance of the acrylic resin complete denture base. *J Prosthet Dent* 1985;54:75-8.
10. Vallittu PK. A review of methods used to reinforce polymethyl methacrylate resin. *J Prosthodont* 1995;4:183-7.
11. Sehajpal SB, Sood VK. Effect of metal fillers on some physical properties of acrylic resin. *J Prosthet Dent* 1989;61:746-51.
12. Asar NV, Albayrak H, Korkmaz T, Turkyilmaz I. Influence of various metal oxides on mechanical and physical properties of heat-cured polymethyl methacrylate denture base resins. *J Adv Prosthodont* 2013;5:241-7.
13. Guo Z, Tan L. Fundamentals and applications of nanomaterials. Artech House; 2009.

14. Wang R, Kayacan R, Küçükeşmen C. Nanotubes/polymethyl methacrylate composite resins as denture base materials. *Carbon Nanomater Biomed Appl* 2016;227-40.
15. Wang R, Tao J, Yu B, Dai L. Characterization of multiwalled carbon nanotube-polymethyl methacrylate composite resins as denture base materials. *J Prosthet Dent* 2014;111:318-26.
16. Yu W, Wang X, Tang Q, Guo M, Zhao J. Reinforcement of denture base PMMA with ZrO₂ nanotubes. *J Mech Behav Biomed Mater* 2014;32:192-7.
17. Abdallah RM. Evaluation of polymethyl methacrylate resin mechanical properties with incorporated halloysite nanotubes. *J Adv Prosthodont* 2016;8:167-71.
18. Shirkavand S, Moslehifard E. Effect of TiO₂ Nanoparticles on Tensile Strength of Dental Acrylic Resins. *J Dent Res Dent Clin Dent Prospects* 2014;8:197-203.
19. Ahmed MA, El-Shennawy M, Althomali YM, Omar A. Effect of titanium dioxide nano particles incorporation on mechanical and physical properties on two different types of acrylic resin denture base. *World J Nano Sci Eng* 2016;6:111-9.
20. Li Z, Sun J, Lan J, Qi Q. Effect of a denture base acrylic resin containing silver nanoparticles on *Candida albicans* adhesion and biofilm formation. *Gerodontology* 2016;33:209-16.
21. Wady AF, Machado AL, Zucolotto V, Zamperini CA, Berni E, Vergani CE. Evaluation of *Candida albicans* adhesion and biofilm formation on a denture base acrylic resin containing silver nanoparticles. *J Appl Microbiol* 2012;112:1163-72.
22. Elshereksi NW, Ghazali MJ, Muchtar A, Azhari CH. Perspectives for titanium-derived fillers usage on denture base composite construction: A review article. *Advances in Materials Science and Engineering* [Internet]. Hindawi Limited; 2014;2014:1-13. Available from: <http://dx.doi.org/10.1155/2014/746252>
23. Bavykin DV, Walsh FC. Titanate and titania nanotubes: Synthesis, properties and applications. 1st ed., Cambridge, UK: Royal Society of Chemistry, (RCS Nanoscience & Nanotechnology). 2010.
24. Kasuga T, Hiramatsu, Hoson A, Sekino T, Niihara K. Formation of titanium oxide nanotube. *Langmuir* 1998;14:3160-3.
25. Indira K, Kamachi Mudali U, Nishimura T, Rajendran N. A review on TiO₂ nanotubes: influence of anodization parameters, formation mechanism, properties, corrosion behavior, and biomedical applications. *J Bio Tribo Corros* 2015;1:28.
26. Jia Y, Kleinhammes A, Kulkarni H, McGuire K, McNeil LE, Wu Y. Synthesis and characterization of TiO₂ nanotube/hydroquinone hybrid structure. *J Nanosci Nanotechnol* 2007;7:458-62.
27. Jia Y, Kleinhammes A, Kulkarni H, McGuire K, McNeil LE, Wu Y. Synthesis and characterization of TiO₂ nanotube/hydroquinone hybrid structure. *J Nanosci Nanotechnol* 2007;7:458-62.
28. Michele TB, Joseph EM, Mathew B, Rowan B, Gun'ko. YK, Horváth E, Zoltán K, Kukovecz A, Imre K, Jonathan NC. Chemical functionalisation of titania nanotubes and their utilisation for the fabrication of reinforced polystyrene composites. *J Mater Chem* 2007;17:2351-8.
29. Porras R, Bavykin DV, Zekonyte J, Walsh FC, Wood RJ. Titanate nanotubes for reinforcement of a poly(ethylene oxide)/chitosan polymer matrix. *Nanotechnology* 2016;27:195706.
30. Khaled SM, Miron RJ, Hamilton DW, Charpentier PA, Rizkalla AS. Reinforcement of resin based cement with titania nanotubes. *Dent Mater* 2010;26:169-78.
31. Dafar MO, Grol MW, Canham PB, Dixon SJ, Rizkalla AS. Reinforcement of flowable dental composites with titanium dioxide nanotubes. *Dent Mater* 2016;32:817-26.
32. Khaled SM, Charpentier PA, Rizkalla AS. Synthesis and characterization of poly(methyl methacrylate)-based experimental bone cements reinforced with TiO₂-SrO nanotubes. *Acta Biomater* 2010;6:3178-86.
33. Hamouda IM, Beyari MM. Addition of glass fibers and titanium dioxide nanoparticles to the acrylic resin denture base material: comparative study with the conventional and high impact types. *Oral Health Dent Manag* 2014;13:107-12.
34. Sodagar A, Bahador A, Khalil S, Shahroudi AS, Kassaei MZ. The effect of TiO₂ and SiO₂ nanoparticles on flexural strength of poly (methyl methacrylate) acrylic resins. *J Prosthodont Res* 2013;57:15-9.
35. Eslami H, Moztarzadeh F, Jafarzadeh Kashi TS, Khoshroo K, Tahri M. Hydrothermal synthesis and characterization of TiO₂-derived nanotubes for biomedical applications. *Synth Reactivity Inorg Met-Org Nano-Met Chem* 2016;46:1149-56.
36. ISO 20795-1. Dentistry - Base polymers - Part 1: Denture base polymers. 2013.
37. Gandhi N, Daniel S, Benjamin S, Kurian N, Varghese VS. Evaluation of surface microhardness following chemical and microwave disinfection of commercially available acrylic resin denture teeth. *J Clin Diagn Res* 2017;11:ZC87-ZC91.
38. Mathew M, Shenoy K, Ravishankar K. Vickers hardness and specific wear rate of poly propylene reinforced PMMA. *Int J Sci Study* 2014;2:71-5.
39. Khoshroo K, Jafarzadeh Kashi TS, Moztarzadeh F, Eslami H, Tahri M. The influence of calcination temperature on the structural and biological characteristics of hydrothermally synthesized TiO₂ nanotube: In vitro study. *Synth Reactivity Inorg Met-Org Nano-Met Chem* 2016;46:1189-94.
40. Edwin TM, Reuben S, Vincent ON, Patrick GN. Multiwalled carbon nanotube-titania nanocomposites: Understanding nano-structural parameters and functionality in dye-sensitized solar cells. *S Afr J Chem* 2015;68:153-64.
41. Bagheri S, Shamel K, Abd Hamid SB. Synthesis and characterization of anatase titanium dioxide nanoparticles using egg white solution via Sol-Gel method. *J Chem* 2013;848205
42. Yu JC, Zhang L, Zheng Z, Zhao J. Synthesis and characterization of phosphated mesoporous titanium dioxide with high photocatalytic activity. *Chem Mater* 2003;15:2280-6.
43. Zhang S, Peng LM, Chen Q, Du GH, Dawson G, Zhou WZ. Formation mechanism of H₂Ti₃O₇ nanotubes. *Phys Rev Lett* 2003;91:256103.
44. Zappini G, Kammann A, Wachter W. Comparison of fracture tests of denture base materials. *J Prosthet Dent* 2003;90:578-85.
45. Hill RG, Bates JF, Lewis TT, Rees N. Fracture toughness of acrylic denture base. *Biomaterials* 1983;4:112-20.

46. Al-Haddad A, Vahid Roudsari R, Satterthwaite JD. Fracture toughness of heat cured denture base acrylic resin modified with Chlorhexidine and Fluconazole as bioactive compounds. *J Dent* 2014;42:180-4.
47. Mecholsky JJ Jr. Fractography: determining the sites of fracture initiation. *Dent Mater* 1995;11:113-6.
48. Soderholm KJ. Review of the fracture toughness approach. *Dent Mater* 2010;26:e63-77.
49. Stafford GD, Huggett R, Causton BE. Fracture toughness of denture base acrylics. *J Biomed Mater Res* 1980;14:359-71.
50. Feng P, Gao C, Shuai C, Peng S. Toughening and strengthening mechanisms of porous akermanite scaffolds reinforced with nano-titania. *RSC Adv* 2015;5:3498-507.
51. Arash B, Wang Q, Varadan VK. Mechanical properties of carbon nanotube/polymer composites. *Sci Rep* 2014;4:1-8.
52. Salehian H, Jenabali Jahromi SH. Effect of titanium dioxide nanoparticles on mechanical properties of vinyl ester-based nanocomposites. *J Compos Mater* 2015;49:2365-73.