Research article

Effect of Bleaching Containing Polydopamine and Chitosan-Modified TiO_2 on the Level of Brightness and Microhardness of Teeth

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Abstract

Teeth bleaching techniques generally use high concentrations of bleaching agents such as H_2O_2, which can harm dental health. Therefore, an alternative method is needed to minimize the use of H_2O_2. The aim of this study was to determine the characteristics and effectiveness of a teeth-whitening gel made from polydopamine and chitosan-modified TiO_2. The research phase began with the extraction of TiO_2 from Tulungagung sand using the leaching method, and then the TiO_2 was modified with polydopamine and chitosan. XRD, FTIR, and TEM were used to characterize the fabrication results. The results of XRD analysis showed that the diffraction peaks of polydopamine and chitosan-modified TiO_2 had the characteristics of anatase phase TiO_2. Functional groups of polydopamine and chitosan-modified TiO_2 were identified from the results of FTIR analysis. The TEM image showed the spherical shape with a core-shell structure, where the TiO_2 particles were covered with polydopamine and chitosan. The addition of H_2O_2 at 3% to the polydopamine and chitosan-modified TiO_2 gel transformed it into a tooth whitening agent. After that, the teeth without soaking and those soaked in cola were bleached with the whitening gel using visible light irradiation three times for 15 min each time. The bleaching results showed that the 0.25-g polydopamine-modified TiO_2 formula whitening gel effectively whitened teeth without causing a significant change in the microhardness value of the tooth surfaces, even at low concentrations of H_2O_2.

Keywords

bleaching;

microhardness;

brightness level

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1. Introduction

Dental treatment with bleaching procedures is a conservative method that has been well-accepted by patients and has been confirmed to be the safest and most effective compared to dental procedures either by direct or indirect restoration of tooth color [1, 2]. Teeth bleaching can be done at home or in an orthodontic clinic [3, 4]. At the office, the bleaching chemicals are used in high concentrations to shorten treatment time. On the other hand, home bleaching at a low concentration of 10% is used. Dental bleaching at home may require treatment for extended periods, for example, 4-8 h a day for 14 days or more [5]. Although the home whitening treatment is the most commonly used method, some patients prefer teeth whitening to be performed in a clinic, where the results are quicker [3]. The active component of most whitening products is hydrogen peroxide (H_2O_2). Although the use of H_2O_2 provides optimal results on both vital and non-vital teeth, there are some concerns regarding extensive whitening techniques. This is because H_2O_2 action on tooth surfaces [6] is triggered by free radicals [7], which can cause tooth oversensitivity and changes in enamel structure, such as changes in hardness and micro-roughness of the teeth [7], as well as injuries to the gums [8, 9].

Therefore, to minimize side effects due to higher concentrations of H_2O_2 (30-35%), alternative materials that have the potential to whiten teeth, such as TiO_2 nanoparticles, are needed [10]. TiO_2 was previously extracted from Tulungagung ilmenite sand, which was known to contain TiO_2 at 12.2% [11]. The advantage of the use of the leaching method in the synthesis of TiO_2 from Tulungagung ilmenite sand, as described by Rohmawati *et al*. [12], was a simple method that did not have a high temperature roasting step. Magnetic and non-magnetic materials from ilmenite sand were separated using a magnetic bar. The result of the separation was a magnetic material that was then dissolved with sulfuric acid. The extraction products from ilmenite sand were 100% anatase TiO_2 without any impurities. TiO_2 phase could be obtained from ilmenite sand by the use of hydrothermal method with NaOH solvent [13] and the caustic fusion method with hydrochloric acid solvent [14]. However, impurities still remained after the use of both methods. Apart from the simplicity of the hydrothermal leaching method used for synthesizing TiO_2 anatase mentioned above, there is also an abundance of sand that has yet to be utilized optimally because so far it has only been used as a building material in the area.

Titanium dioxide (TiO_2) is a nontoxic biocompatible compound that possesses antimicrobial properties [15, 16]. Over the last few decades, researchers have focused on TiO_2 because of its nature as a photocatalyst and because of its many potential applications in the biomedical field [17]. TiO_2 nanoparticles affect the efficiency of whitening agents without reducing the hardness of the tooth enamel surface [18]. Bleaching teeth with visible light irradiation using a concentration of 35% H_2O_2 is less effective in whitening teeth when compared to the use of a 35% H_2O_2 formula and TiO_2 with UV light irradiation [19] because when TiO_2 is exposed to UV light, it actively forms free radicals [16]. The photocatalyst properties of TiO_2 nanoparticles can increase with prolonged use of UV. However, the clinical use of UV light for teeth whitening has undesirable effects [20]. Long-term exposure to UV radiation results in toxic irritation that leads to cell damage, immune suppression, skin cancer, and photoaging [21], as well as causing problems in soft tissues, including the oral mucosa [22, 23].

Zhang *et al*. [24] reported that using visible light for 30 min was a solution to replace UV light with an additional 30% H_2O_2. The research results provided a white effect, but damage occurred to tooth enamel due to high levels of H_2O_2. Likewise, a concentration of 6% H_2O_2 in a TiO_2 solution for 45 min in visible light showed a white effect, but the teeth experience over-bleaching, eroding the enamel [8]. Suemori *et al*. [25] carried out tooth whitening from TiO_2 with the addition of 3.5% H_2O_2, each activated by 405 nm diode laser light and halogen lamp for 15 min, showing a level of tooth brightness without damaging the enamel. Sun *et al*. [26] described that the

photocatalytic activity of TiO_2 anatase in visible light could be improved by modifying it with polydopamine.

Polydopamine (PDA) has been used in various applications because it is considered a natural biopolymer [27]. PDA is a polymer that can be applied in several materials, such as metals, metal oxides, non-metal oxides, silica, ceramics, polymers, and other nanomaterials [28]. PDA has optical properties related to its absorption of ultraviolet (UV) light and visible light [27], and can be used with TiO_2 to improve catalysis in short irradiation process. Zhang *et al*. [24] reported that PDA-modified nano TiO_2 can increase the brightness of the teeth. The results of their study show that when the sample is still in the form of powder, it is less efficient at teeth whitening. Teeth whitening gel with 6% H_2O_2, including TiO_2 and chitosan, provided compelling whitening without negative effects on the roughness or hardness of the tooth surface [15]. Chitosan is an alternative remineralizing teeth agent that is of low cost [29] and does not irritate the gums [30]. Chitosan is a natural polysaccharide, non-toxic, biocompatible, and biodegradable.

Chitosan is widely used in biomedical, food, cosmetic, and pharmaceutical applications because of its film and gel-forming capabilities. It is also bioactivity and used as bioadhesive. Moreover, it possesses remineralizing and antibacterial characteristics [31-33]. Chitosan was used in experimental gel whitening agents as an alternative to synthetic polymers. It functions as a thickener, carrier, bioadhesive, demineralizing, antioxidant, and antimicrobial [15]. In addition, chitosan-modified TiO_2 displays a combination of the photocatalytic properties of nano TiO_2 and the adsorption properties of chitosan, making it very appropriate and adequate for bleaching care [34]. Li *et al*. [35] described that adding 0.05-0.2% chitosan expanded the brightness of the Kraft pulp. Based on information from several researchers above, this research fabricated PDA and chitosan-modified TiO_2 with 3% H_2O_2 as a tooth whitener, which can later be developed into a home dental care product. So far, the use of PDA and chitosan-modified TiO_2 and 3% H_2O_2 has never been reported. Thus, in this research, the influence of PDA and chitosan-modified TiO_2 with 3% H_2O_2 on the brightness level and microhardness of the teeth was determined and the results of this teeth whitening product are expected to be effective in brightening teeth and does not damaging the teeth.

2. Materials and Methods

2.1 Materials

The materials used in the manufacture of PDA and chitosan-modified TiO_2 were Tulungagung Ilmenite sand, H_2SO_4 (Sigma Aldrich 99%), dopamine hydrochloride (Sigma Aldrich 99%), hexamethylenetetramine (Sigma Aldrich 99%), NaOH (Merck), CH_3COOH (Merck), ethanol (Merck), distilled water, cola, and molar teeth. Equipment for the experimental process included beakers, a digital Ohaus balance, measuring cups, laboratory spatula, mortar and pestle, 200 mesh sieves, a vacuum pump, a glass filtration unit, hot plates, Buchner funnels, a drying oven, and a furnace.

2.2 Synthesis of anatase TiO_2

TiO_2 manufacture was based on the method of Rohmawati *et al*. [12] by the use of the hydrothermal leaching method. This involved pulverizing ilmenite sand using a mortar and pestle and then sifting the sand to a size of 200 mesh. After that, the sand was dissolved in 8 M H_2SO_4 and stirred using a magnetic stirrer at 700 rpm at 120ºC. The solution formed a slurry and the $TiOSO_4$ filtrate and $FeSO_4$ precipitate were then separated using a vacuum pump. The filtrate from the separation was added to distilled water and heated at 300°C for 12 h. The precipitate formed by the heating process

was washed with distilled water several times until its pH was 7. The solution was then filtered, and the residue was calcinated at 600°C for 2 h. A dry powder was then obtained. The stages of the anatase TiO_2 synthesis process are illustrated in Figure 1.

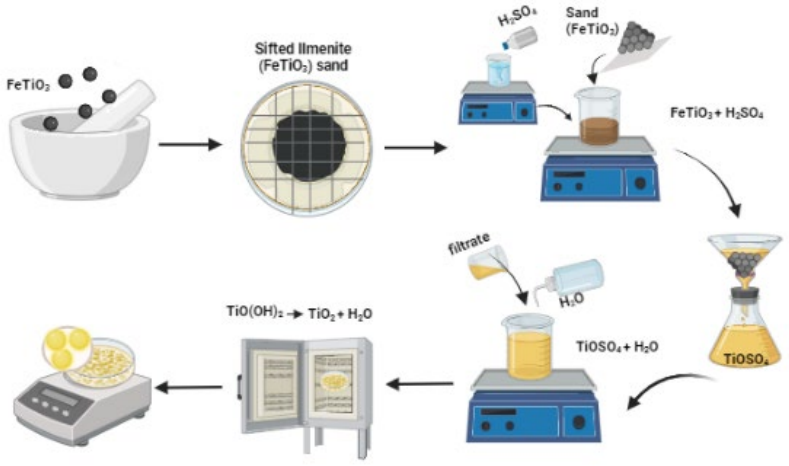


Figure 1. Preparation process for the synthesis of TiO_2 from Tulungagung ilmenite

2.3 Fabrication of polydopamine and chitosan-modified TiO_2

A mass of TiO_2 of 0.08 g and a mass of dopamine of 0.04 g were mixed with distilled water and stirred until a suspension was formed [36]. Then, 0.1 g of hexamethylenetetramine (HMTA) was added to the solution using the sonication method. The solution was then dried at 90°C for 3 h in a drying oven; then, the solution was centrifuged at 4000 rpm to produce precipitates. Next, the precipitate was washed with distilled water and ethanol to acquire a wet precipitate. After that, it was dried in the drying oven at 80ºC for 30 min and PDA-modified TiO_2 was obtained (Figure 2).

In the next stage, 0.2 g of chitosan was first dissolved in 7 mL of acetic acid and 25 mL of distilled water. Then, 0.05 g of PDA-modified TiO_2 was added. After that, the mixture was stirred at 60ºC with a speed of 500 rpm and 0.1 M NaOH was added until the pH solution was 7, and the brownish-colored gel obtained. In the next stage, 3% H_2O_2 was added to the gel and stirred until homogeneous. The above steps were repeated for PDA-modified TiO_2 with a mass of 0.25 g. The detailed stages of fabrication of PDA and chitosan-modified TiO_2 can be seen in Figure 3.

2.4 Characterization

TiO_2, PDA-modified TiO_2, and PDA and chitosan-modified TiO_2 samples from the synthesis were characterized by XRD (X-ray diffraction) to determine the diffraction patterns of the anatase TiO_2 phase and changes in the TiO_2 crystal structure due to modification with PDA and chitosan. The XRD device used was a Philips X'Pert MPD system with a Cu anode radiation source of 40 kV, 30 mA, and a wavelength of CuKα of 1.54056 Å at an angle of 2 theta 10-90°. In addition, FTIR (Fourier transform infrared spectrophotometry) was also performed to determine the functional groups of the fabricated samples. FTIR results were recorded on a Shimadzu-type IR Prestige 21 instrument with a 4000-500 cm^{-1} wavenumber range. TEM (transmission electron microscopy) (Tecnai G2 20S-Twin Function type) was performed to determine the morphology and the particle size of PDA and chitosan-modified TiO_2 samples and ImageJ software was used.

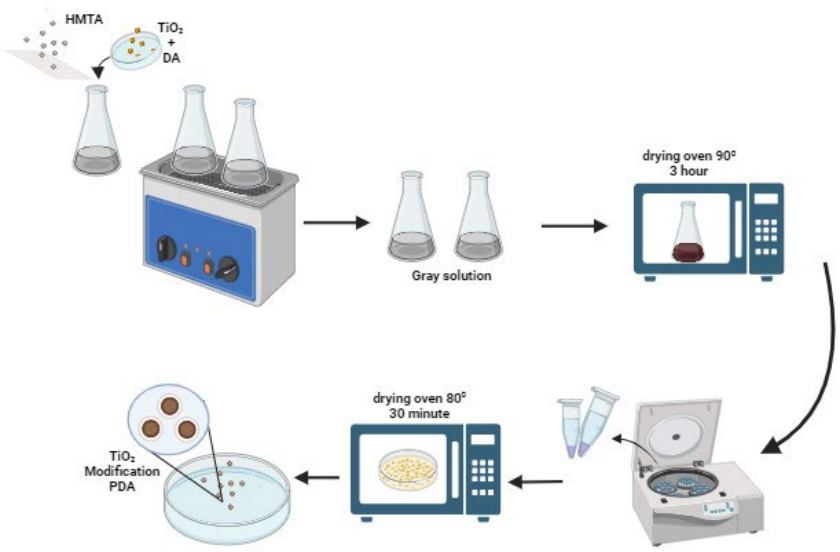


Figure 2. Preparation of TiO_2 by modified polydopamine

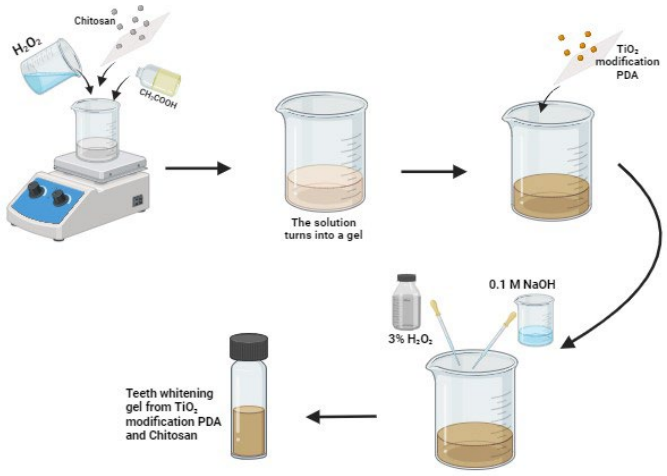


Figure 3. Fabrication of polydopamine and chitosan-modified TiO_2

Teeth with and without cola immersion underwent bleaching. The bleaching result was then measured at the brightness level using a UV-vis spectrophotometer (Ultraviolet-visible spectroscopic PC-2401). The data obtained from spectrophotometer were calculated for color parameters at distances L*, a*, b*, based on the CIELAB system created in 1978 by the Commission International de I'Eclairage (CIE). The CIELAB system explains color perception in three dimensions. The L* value denotes the brightness level of the teeth (light or dark), a* in color analysis represents the red-green level, and b* defines the yellow-blue level. The level of tooth microhardness after bleaching was determined by a Vickers hardness test (HV) on a Mitutoyo HM

200. Before the microhardness test, the teeth were cut in half from the tooth crown and then coated with resin as an adhesive during the test. The hardness test was conducted for 20 s with a loading force of 0.1 N to appraise superficial <5 µm subsurface enamel [37]. The level of surface abrasion of tooth enamel was determined using a scanning electron microscope (Zeiss EVO MA10) with a voltage range of 0.2 to 30 kV.

3. Results and Discussion

3.1 X-ray diffraction (XRD)

In this study, XRD characterization was carried out to determine the structure of the main phase in the synthesized sample, and Match! software was used for data analysis. The sample diffraction spectra in Figure 4 shows that each peak indicates the main phase of TiO_2 anatase according to JCPDS (Joint Committee on Powder Diffraction Standards) Number 96-900-8216. The diffraction peaks are 25.28, 37.58, 47.86, 53.59, 54.90, 62.33, 68.40, 74.86, 82.28 with the Miller index (101), (004), (020), (015), (121), (024), (116), (125), (224), respectively, which together characterize the anatase phase. The highest diffraction peak in-plane orientation (101) was located at an angle of 25.28°, which was in agreement with the results of Saranya *et al*. [38] and Kalaiarasi and Jose [39], who reported angles of 25.25° (101) and 25.3° (101), respctively. The diffraction peaks for the PDA-modified TiO_2 sample show the characteristics of the anatase TiO_2 phase. The peaks are similar to the standard TiO_2 diffraction pattern peaks, so the addition of PDA had no impact on the TiO_2 crystal structure. Likewise, the diffraction pattern of the PDA and chitosan-modified TiO_2 samples did not show a change in TiO_2 crystallinity; however, the intensity of the diffraction peaks changed due to the presence of H bonds between chitosan and TiO_2 [40]. The chitosan diffraction peaks were not found in the diffraction patterns of PDA and chitosan-modified by TiO_2 samples. Ths indicated that bonds between chitosan, polydopamine, and TiO_2 had formed.

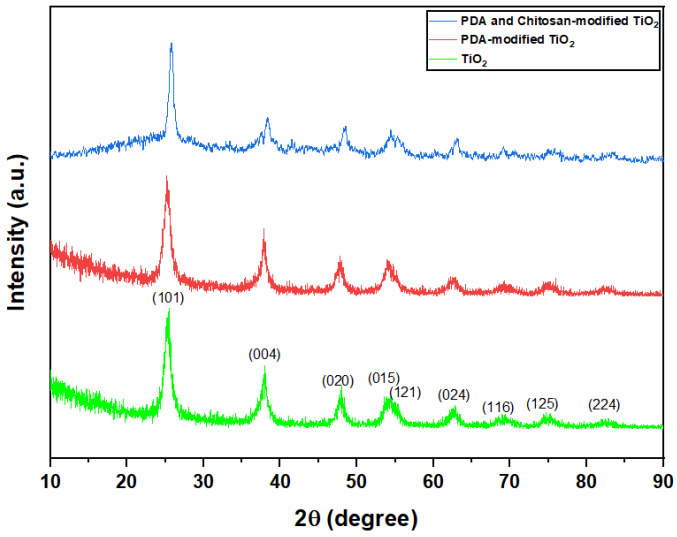


Figure 4. Diffraction patterns of PDA-modified TiO_2 and PDA-chitosan-modified TiO_2 against standard TiO_2

3.2 Fourier transform infrared spectrophotometry (FTIR)

The FTIR characterization was used to identify groups of chemical bonds in the TiO_2 samples, PDA-modified TiO_2 (TiO_2-PDA), and PDA and chitosan-modified TiO_2 (TiO_2-PDA-chitosan). The data from the test results in Figure 5 shows the absorption peaks over the wavenumber range 4000-500 cm^{-1}. The experimental sample peaks were identified by matching them with reference data, as detailed in Table 1. The TiO_2 samples synthesized from ilmenite sand in the Tulungagung coastal area contained organic compounds that usually occur in seawater organisms, one of which was detected in the FTIR spectrum in Figure 5(a), with absorption peaks at 1180.44 and 1114.86 cm^{-1}, propably indicating an alkyl halide compound [41]. At wavenumber 1055.06 cm^{-1}, an absorption peak which indicated O-H stretching vibrations was observed. This was probably was due to the presence of absorbed water and hydroxyl groups [42]. The Ti-O stretching and Ti-O-Ti peaks, characteristics of TiO_2 anatase, were found at 935.48, 825.53, and 754.17 cm^{-1}.

Figure 5(b) shows the spectrum of the PDA-modified TiO_2 sample where the absorption peaks at 935.48 and 771.53 cm^{-1} indicate the functional groups of TiO_2 anatase. The characteristic peaks of PDA are at wave numbers of 1456-1058 cm^{-1}. These corresponded to the functional groups of C-C, CH_2 scissoring, C–O symmetry stretching vibration, C-O vibration, and C-H plane bending vibration. The TiO2-PDA-chitosan sample in Figure 5(c) showed absorption peaks at 3642.25 and 3562.52 cm^{-1}, showing hydrogen bonds between the –H bonded hydroxyl groups due to the absorption of H_2O [43]. Group of C=O stretching in the amide I was identified at wavenumbers of 1990.54, 1687.7, 1643.35, and 1614.42 cm^{-1}, which were wavenumber characteristics of chitosan [44]. The attributes of PDA were identified at 1091.7 cm^{-1} in the C-H functional group. The absorption peaks at 590.22, and 540.07 cm^{-1} indicated groups belonging to TiO_2 [45]. Therefore, the results of the FTIR analysis above showed that the functional group of PDA and chitosan-modified TiO_2 samples were identified where each absorption peak shows the characteristics of polydopamine and chitosan-modified TiO_2.

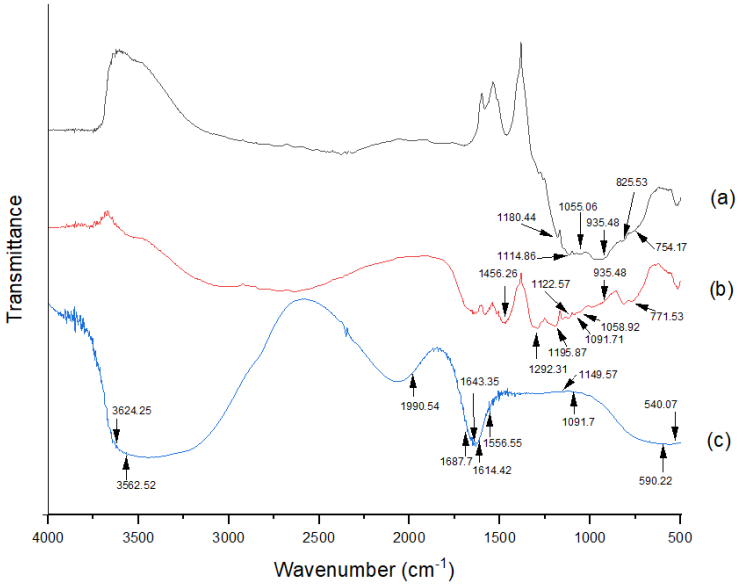


Figure 5. The FTIR transmittance spectra of the samples (a) TiO_2 (b) PDA-modified TiO_2 (c) PDA and chitosan-modified TiO_2

Table 1. Functional groups on FTIR wavenumbers

Sample	Wavenumber (cm^{-1})		Functional Group
	Experiment	Reference	
TiO_2	1180.44, 1114.86	1104 [41]	Alkyl halide
	1055.06	1078 [42]	O-H stretching vibrations
	935.48, 825.53, 754.17	1000-400 [46]	Ti-O stretching, Ti-O-Ti bridging stretching
PDA-modified TiO_2	1456.26	1450 [47]	C-C
	1292.31	1288 [48]	CH_2 scissoring
	1195.87	1184 [49]	C–O symmetry stretching vibration
	1122.57	1120 [50]	C-O vibration
	1091.71, 1058.92	1065 [51]	C-H plane bending vibration
	935.48, 771.53	1000-400 [46]	Ti-O stretching, Ti-O-Ti bridging stretching
PDA and chitosan-modified TiO_2	3642.25, 3562.52	3700-3420 [43]	-H bonded hydroxyl group
	1990.54, 1687.7, 1643.35, 1614.42	1645 [44]	C=O stretching of amide I
	1556.55	1550 [44]	N–H bending in amide II
	1149.57	1153 [52]	Asymmetric stretching C-O-C
	1091.7	1065 [51]	C-H plane bending vibration
	590.22	740.67 [44]	Ti–O vibration
	540.07	609.51, 516.92 [45]	TiO_2 stretching

3.3 Transmission electron microscopy (TEM)

The morphology and coating forms of PDA and chitosan-modified TiO_2 samples and the particle size of the composite was observed using TEM, as shown in Figure 6. The particle size distribution was determined by Image J software, and the analysis was based on the number of 100 grains.

Figure 6 shows that the PDA and chitosan-modified TiO_2 samples have a core-shell structure. The PDA and chitosan-modified TiO_2 particles were of spherical shape. These results were in alignment with the research of Zhang *et al*. [24], who synthesized a PDA-modified nano TiO_2 (nano-TiO_2@PDA) material that had a particle size of 40 nm and particle size thickness of about 2 nm. In our study, the TEM analysis in Figure 7 clearly shows that the shape of the TiO_2 particles covered by polydopamine and chitosan had a particle core size of 70.63 nm, while an organic surface layer (shell) had a surface thickness of 7.62 nm. An increased TiO_2 particle size may be caused by TiO_2 agglomeration occurring with an irregular size distribution [53]. Thus, the PDA and chitosan-modified TiO_2 in our study can be considered a nano material because of its size of ≤100 nm.

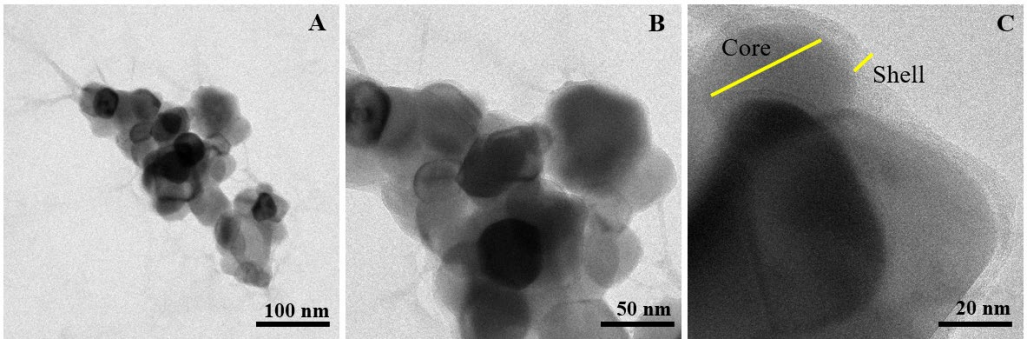


Figure 6. Micrograph of TiO_2-PDA-chitosan sample

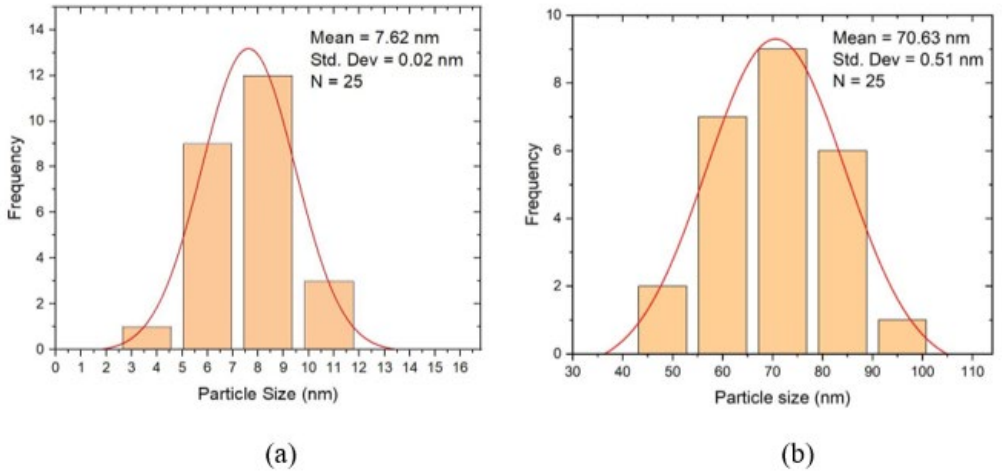


Figure 7. Particle size distribution of PDA and chitosan-modified TiO_2 (a) shell size (b) core size

3.4 Tooth brightness level using the PC-2401 UV-vis spectrophotometer

The results of the teeth bleaching process using PDA and chitosan-modified TiO_2 formulas with 3% H_2O_2 and containing 0.25 g and 0.05 g, are shown in Table 2. The samples were bleached 3 times for 15 min under visible light irradiation, and applied to the tooth surface. Brightness level of the teeth was determined using the UV spectrophotometer. The value of tooth brightness (L*) before bleaching was 112.34 for the tooth sample without cola immersion, whereas after bleaching with the formula 0.05-g tooth whitening gel, it became 112.96. Likewise, teeth soaked in cola had a brightness level of 103.67 before bleaching, while after bleaching, the 0.05-g formula whitening gel gave a brightness of 112.48. The results obtained from the 0.25 g of whitening gel formula showed significant brightness with and without immersion treatment in cola, namely 121.77 and 121.25.

When TiO_2-based tooth whitening gel adheres to colored tooth enamel and is exposed to blue visible light, its TiO_2 becomes photocatalytically active. The photon energy absorbed by TiO_2 causes electrons to be excited into a conduction band, thereby reducing oxygen levels and causing

Table 2. The results of quantitative test of tooth brightness using UV-vis PC

Sample	Condition	Teeth Whitening Gel Content (g)	Teeth Color Test Value			
			L*	a*	b*	dE*ab
Teeth without cola soak	Before bleaching	-	112.34	-0.62	0.06	0.00
	After bleaching	0.05	112.96	-1.01	- 1.23	1.48
		0.25	121.77	-2.87	-4.75	10.82
Teeth with cola soak for 7 days	Before bleaching	-	103.67	-0.94	-1.19	0.00
	After bleaching	0.05	112.48	-2.78	-10.12	12.67
		0.25	121.25	-4.84	-10.61	20.32

production of superoxide radicals (O_2^-), while holes formed in the valence band cause a decrease in hydroxide ions and the production of hydroxyl radicals (OH^-). These free radicals can modify organic compounds such as chromogens that cause discoloration of teeth through oxidation and degradation processes [10], in which the chromogen molecules are degraded into smaller, transparent, and soluble molecules, removing stains and whitening teeth [54]. Teeth whitener can produce free radicals even though it only uses a concentration of 3% H_2O_2 [10]. The addition of PDA in this research likely increased the catalytic activity of TiO_2, especially during the bleaching process using visible light [24]. Moreover, the addition of chitosan can combine the photocatalytic properties of nano TiO_2 and the adsorption properties of chitosan, so it is a suitable and effective additive for whitening treatments [15, 34] and it can even increase the adhesion of the gel onto the tooth surface, thereby stabilizing and even preventing the release of free radicals [35]. In addition, chitosan can also function as a thickener, bioadhesive, and remineralization agent [15]. However, using high catalyst concentrations is not recommended because such concentrations can disrupt the aggregation of catalyst particles, significantly reducing photocatalytic activity [55-57].

The tooth brightness value obtained in this study was greater than that of Suemori *et al*. [25], who used TiO_2 and 3.5% H_2O_2 and Ozcetin and Surmelioglu [15], who examined a formula with TiO_2/chitosan/6% HP. In Suemori *et al*. [25], a TiO_2 formula and 3.5% H_2O_2 were used for bleaching under visible light, as was done in this study. Their obtained data were processed with the Tukey test including the highest brightness of 72.24^{cd} after visible light irradiation produced by a 405 nm diode laser, whereas under a halogen lamp (320-1100 nm), the teeth had a brightness of 71.04^{cd}. Ozcetin and Surmelioglu [15] used tooth whitening gel under UV light (< 385 nm) to form free radicals with a brightness of 90.5±5.1. However, continuous UV irradiation has an unfavorable effect around the teeth [58]. PDA and chitosan-modified TiO_2 can increase the brightness of the teeth, even though the bleaching process is carried out by irradiating visible light. This is because PDA and chitosan-modified TiO_2 can produce free radicals that degrade the color of teeth, making them appear whiter and brighter [59].

Teeth whitening in this study was repeated thrice every 15 min. For each repetition, the teeth were cleaned and dried, then bleached again for 15 min. The effect of bleaching on tooth brightness was observed for each repetition, both for teeth with and without cola soaking treatment. The length of exposure during the bleaching process can increase the photocatalytic activity of the teeth-whitening gel, producing many free radicals. However, the effect of prolonged exposure can increase the temperature along with the penetration of H_2O_2, resulting in an increase in pulp temperature and causing the teeth to become sensitive [60].

3.5 Microhardness of teeth

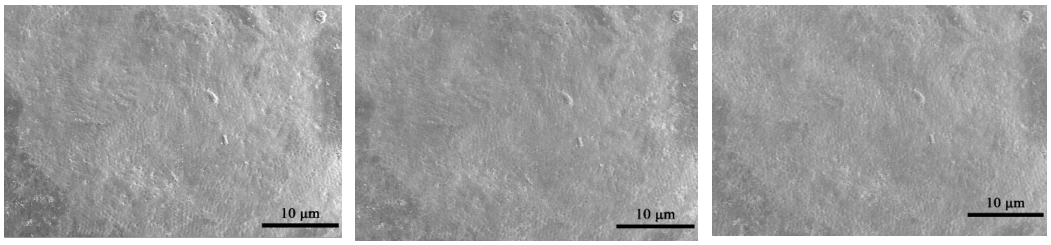
Tooth samples that had gone through the bleaching process were subjected to the Micro–Vickers hardness test to determine the hardness of the teeth. The Micro-Vickers test was applied using a loading force of 0.1 N to determine the subsurface hardness of superficial enamel <5 μm. microhardness test results data can be seen in Table 3 for teeth before and after the bleaching process, both for teeth without cola immersion and teeth with cola immersion.

Table 3. Microhardness values before and after the bleaching process

Teeth Sample	Condition	Teeth Whitening Gel (g)	Microhardness (HV)
Teeth without cola soak	Before bleaching	-	16.67
	After bleaching	0.05	16.27
		0.25	16.13
Teeth with cola soak for 7 days	Before bleaching	-	26.17
	After bleaching	0.05	25.43
		0.25	25.20

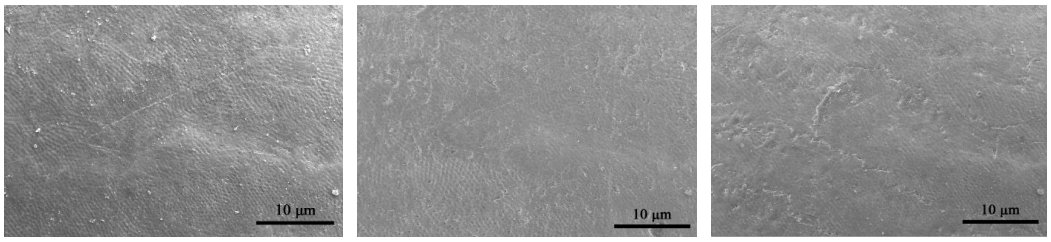
The results of the study presented in Table 3 show the microhardness of the teeth samples without immersion and with cola immersion for 7 days. Before the bleaching process, the teeth without cola immersion were tested for microhardness, and a microhardness value of 16.67HV was obtained. However, after the bleaching process, the microhardness of teeth after being smeared with the 0.05-g whitening gel material was 16.27 HV. Similarly, for 0.25-g whitening gel material, the tooth microhardness obtained was 16.13 HV. In the next test, teeth soaked in cola for 7 days were studied. Teeth were immersed to the roots and the hardness and abrasion of the teeth was evaluated. Based on the hardness test results, teeth soaked in cola before bleaching had a hardness of 26.17 HV. After bleaching and using a composition of 0.05 g and 0.25 g of teeth-whitening gel formulas, microhardness of 25.43 HV and 25.20 HV, respectively, was observed. The tooth hardness test obtained in this study showed low values because the loading force of the test was carried out on the superficial enamel < 5 μm. The use of bleaching agent concentration [61, 62], application time [63], and bleaching agent content [64-66] have been shown to affect microhardness. However, our research suggests that teeth without cola immersion did not show a significant change in microhardness, in contrast with teeth treated with cola immersion, for which microhardness value decreased after the bleaching process, although there was only a slight change. This was probably because the contact period between the cola solution and the teeth over 7 days causes a decrease in pH that had the potential to cause demineralization and erosion of the tooth structure [63]. Furthermore, cola can cause an intense brown discoloration of tooth enamel [67] due to phosphoric acid and chromogen [68]. Phosphoric acid can weaken tooth enamel, causing it to erode and change color quickly due to chromagens [68]. In this study, there was no variation in the length of cola soaking on the teeth, however, cola soaking was carried out for only 7 days. Wang *et al*. [69] stated that during 7 days of soaking with cola, the surface of the teeth experienced discoloration and stains.

The morphology of tooth enamel abrasion before and after bleaching was observed using SEM characterization with 500x magnification. Figure 8 shows the surface morphology of tooth enamel before and after bleaching for teeth without cola immersion. There is slight damage to the tooth enamel, as indicated by the holes in the tooth enamel, as shown in Figure 8 (c). It shows that the free radicals produced by the TiO_2 nanocatalyst and 3% H_2O_2 slightly damaged tooth enamel, affecting tooth hardness. The surface morphology of tooth enamel for cola soaking before bleaching in Figure 9(a) shows tooth enamel erosion in the form of holes and scratches in the tooth area. After the bleaching procedure (Figure 9(b-c)), it is clear that there are sharp scratches on the teeth and tooth enamel is damaged, which could have an impact on the tooth microhardness value.



(a) (b) (c)

Figure 8. Surface morphology of tooth enamel without cola soaking treatment (a) before bleaching (b) after bleaching with 0.05 g tooth whitening gel (c) after bleaching with 0.25 g tooth whitening gel



(a) (b) (c)

Figure 9. Surface morphology of tooth enamel soaked in cola (a) before bleaching (b) after bleaching with 0.05 g tooth whitening gel (c) after bleaching with 0.25 g tooth whitening gel

In ou research, different teeth were used for the treatmentwithout and with cola soaking, and the results of the Micro-Vickers test showed differences in microhardness. It should be noted that this research was focused only on the effects of bleaching using tooth whitening gel on the brightness and microhardness of teeth without and with cola soaking. Each tooth of the same type and treatment was observed for changes in color and hardness value three times after bleaching. The stability of tooth brightness after bleaching in this study has yet to be studied and the study was only focuses on the effects of bleaching on tooth brightness. In subsequent research, the stability of tooth brightness by repeatedly immersing the dye will be examined. Dehydration of teeth after bleaching can occur. The use of high H_2O_2 concentrations of around 25% produces faster tooth whitening [69] but can cause high thermal sensitivity [70], resulting in more dehydration [71, 72]. Lee *et al*. [73] stated that using a low H_2O_2 concentration, namely 3 to 4%, could minimize the level of thermal sensitivity or even cause no thermal sensitivity after the bleaching procedure, which could reduce dehydration. Therefore, using a low concentration as in this study, i.e. 3% H_2O_2, may not impact thermal sensitivity and may reduce tooth dehydration.

4. Conclusions

PDA and chitosan-modified TiO_2 samples were successfully fabricated in this study and had the following characteristics. The diffraction pattern of PDA and chitosan-modified TiO_2 samples showed no change in TiO_2 crystallinity, and the anatase phase was identified. Each absorption peak from the FTIR results shows the characteristics of PDA and chitosan-modified TiO_2. TEM image shows a core-shell structure where the TiO_2 particles are covered with PDA and chitosan. The 3%

H_2O_2 addition to the TiO_2 samples, modified by polydopamine and chitosan, made the material into a gel that could be used as a teeth-whitening agent. The results of three bleaches (each of 15 min) on the tooth surface with a duration under visible light irradiation over a wavelength of 420-480 nm showed that the gel was effective on brightening teeth and did not cause a significant change in the microhardness value of the teeth either with or without cola immersion. For the 0.25 g sample, the PDA-modified TiO_2 was found to produce tooth brightness and tooth microhardness values for teeth without cola immersion of 121.77 and 16.13 HV, respectively, while for teeth with cola immersion, the brightness and hardness values were 121.25 and 25.20 HV, respectively. In our study, a greater concentration of bleach, delivered as a greater content of PDA-modified TiO_2, increased the brightness of teeth, even though H_2O_2 was use at a relatively low concentration.

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