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Research Article

Physical and Chemical Investigation of TiO_2 Nanotubes Treated with Isopropyl Triisostearoyl Titanate (KR-TTS)

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The aim of this study is to investigate the effect of isopropyl triisostearoyl titanate (KR-TTS) as a titanate coupling agent (TCA) on surface modification of TiO_2 nanotube (TNT) material. From the physical and chemical studies that have been performed on the modified TiO_2 nanotube, scanning electron microscope micrographs, energy-dispersive X-ray and viscosity indicated that there was significant reduction in particle aggregation of the modified TiO_2 Nanotube. FTIR spectroscopy confirmed that the functional group of the TCA reacted with the hydroxyl groups present on the surface of TiO_2 nanotube resulting in an altered surface property from being hydrophilic to hydrophobic. X-ray diffraction indicated that crystalline structure did not change upon the modification with the coupling agent. Isopropyl triisostearoyl titanate (KR-TTS) is found to be superior in performance and has a significant effect on the dispersion and resolving of agglomeration. This paper presents the effect of surface modification with the TCA of isopropyl triisostearoyl titanate (KR-TTS) type on the TiO_2 nanotube material.

1. Introduction

The introduction of nanoscale material offers new, promising additives for improvement of the mechanical properties because of their high surface area to volume ratio [1]. Nanotubes consist of long cylinders with a hollow cavity at the center that exhibits increased surface area compared to nanoparticles (NPs) [2]. The aspect ratio of nanotubes is usually more than 10 and it can reach up to several thousand [3]. The surface area of TiO_2 nanotube is about five times higher than the titanium oxide nanoparticle (NP), and it is around $250\,m^2/g$ [4–6].

Nanotitanium oxide (TiO_2) has a wide variety and different applications due to its recognized specifications such as low costs, optical and electronic properties, chemical stability, high photocatalytic activity, nontoxicity, UV protectivity, antibacterial agent, and environmental purification [7–10]. Titanium is a potential material in dental and medical applications due to the excellent bioactivity, biocompatibility, and mechanical properties [6, 11, 12]. This material, which is high in stability, poses great aesthetic capabilities, low toxicity, high efficiency, and abundancy, makes it a favorable antimicrobial additive [6, 13].

Titanium oxide nanotube (TiO_2) has been used recently as a polymer reinforcement and has provided an excellent effect on biomedical compatibility as well as in improving the mechanical properties of acrylic resins [4, 9, 14]. It has been approved from the previous studies that the use of nanotubes additives was a success in the resin-based bone cement and dentals [4]. It also reported that the open-ended tubular structure of the nanotubes may allow the matrix material to enter into the tubes by capillary action and form a stronger composite which leads to increased load transformation [4]. Nonetheless, several studies demonstrated that blank TiO_2 nanotube addition was limited due to its clustering and aggregation which was caused by its high surface energy.

Its tendency for aggregation causes the creation of a weak area and limits its application [15, 16].

The surface modification of materials means grafting of organic coatings on its surface which can be performed with the coupling agent to change the surface from having hydrophilic to hydrophobic properties. It can be carried out by utilizing physical and chemical interactions between the nanomaterial and the modifiers through the creation of a molecular bridges to solve the problems of clustering and aggregation [17–19]. Throughout the research findings, it has been concluded that the titanium coupling agents (TCAs) have more significant properties in treating unlimited types of materials. Researches related to dental applications show that the biocompatibility of TCAs were superior in terms of hydrolytic stability in oral and wet environments [1, 20–22]. This paper presents the TiO_2 nanotube modification with the titanate coupling agent (TCA) of isopropyl triisostearoyl titanate (KR-TTS) type.

2. Experimental Procedure

2.1. Materials. Titanium dioxide (TiO_2) nanotube with an average diameter of 25 nm was provided by Sigma-Aldrich, USA, and specific surface area of 150 m^2/g and molecular weight of 79.9 g/mol were used as the treated material. Isopropyl triisostearoyl titanate (KR-TTS) provided by Kenrich Petrochemicals, USA, was used as the surface treatment material, it is a light brown-reddish liquid with a density of 0.92 g/cm^3 and having a chemical composition of $C_{57}H_{112}O_7Ti$. Toluene (TOL/Sigma-Aldrich, USA, 99.89% purity, 92.14 g/mol molecular weight) as an anhydrous colorless liquid used to mix with isopropyl triisostearoyl titanate (KR-TTS) by a specific percentage, its chemical composition was C_7H_8, and it is used to prevent the hydrolysis of coupling agent near the surface of TiO_2. Also, a colorless liquid material ethyl alcohol (ethanol) provided by Sigma-Aldrich, USA, 95% purity, with a chemical composition of C_2H_6O, molecular weight of 46.07 g/mol, has been used for washing the treated material in order to eliminate the residual titante coupling agent (TCA) and toluene (TOL). Paraffin oil is a viscous liquid provided by Sigma-Aldrich, USA, with a density of 0.861 g/cm^3, used to evaluate the surface modification of the fillers through the viscosity test.

2.2. Surface Modification of TiO_2 Nanotubes. An identified amount of 2.0 g of inorganic TiO_2 nanotube powder has been weighted with four-digit analog balance (MonoBloc, model no. 8303, China). The weighted TiO_2 nanotubes were heated in a vacuumed electrical tube furnace under a temperature of 80°C for 4 hr in order to remove any moisture that may available on the powder surface. To prepare the coupling agent solution, an amount of 2 wt% of isopropyl triisostearoyl titanate (KR-TTS) (relative to the weighted TiO_2 nanotubes) has been added into a beaker containing of (100 mL) of toluene liquid and stirred by the speed of 300 rpm for 30 min, using magnetic stirrer apparatus (INTLLAB MS-500, China). Then, TiO_2 nanotubes have been dispersed in the coupling moisture and stirred by the indicated magnetic stirrer, with a speed of 300 rpm for 1 hr and at room temperature. TiO_2 nanotubes moisture has been filtered from the TCA and toluene liquids by using a centrifugal filter apparatus (Eppendorf Centrifuge 5415 R, Germany) to separate the filler from the moisture followed by filtering with a laboratory filter paper, and then washing by ethanol for three times. The obtained treated TiO_2 nanotubes have been dried with the use of electrical vacuumed tube furnace at 80°C for 6 hr, by placing the powder in the vacuumed quartz tube. After the dryness process, the treated powder has been kept in a vessel. The last drying process of the TiO_2 nanotubes was conducted to perform a complete evaporation of any supposed residual ethanol and toluene.

2.3. TiO_2 Nanotubes Characterizations

2.3.1. Fourier Transform Infrared Spectroscopy (FTIR) Test. Fourier transform infrared (FTIR) is a nondestructive, optical performance inspection used to recognize the grafting of the functional groups of coupling agents into the surface of the TiO_2 nanotubes and its modification. FTIR spectrometer used was Bruker FTIR Alpha Universal sampling module, USA. The testing sample has been prepared with the KBr disk. Materiel has been scanned for 10 times with a wavelength range of 500–4,000 cm^{-1} and a resolution set to 4 cm^{-1}.

2.3.2. X-Ray Diffraction (XRD) Test. X-ray diffraction has been used to characterize the atomic structure of the TiO_2 nanotube, analyzing their crystal structures, and to evaluate if the TCA was altered the filler atomic structure. The XRD diffractometer apparatus Bruker D2 PHASER, XRD powder diffractometer, USA, was used to investigate the crystal structure of the treated TiO_2 nanotube materials, where the measuring range was $2\theta = 5°–90°$ and scanning speed was 10/min.

2.3.3. SEM Investigation. Scanning electron microscope (SEM) has been used for investigating the morphology and agglomeration of the modified material. SEM device used was Zeiss GEMINI SEM 500, Germany, model with a voltage range from 0.2 to 30 kV. The apparatus used was using a focused beam of electrons with a high energy in order to create a variation of signals on the surface of the sample. The obtained signals reflect an indication about the external morphology and the orientation of materials forming the powder.

2.3.4. Viscosity Test. The viscosity test provides an indication on the range of change in viscosity of the treated filler in comparison to the untreated filler. This test has been conducted by mixing of filler with paraffin oil and measuring the moisture viscosity by the viscometer apparatus. Ten grams from each treated and nontreated filler have been immersed individually in a scald container (beaker) of 100 mm diameter containing of 150 mL liquid paraffin and mixing the filler with the paraffin by a magnetic stirrer of 300 rpm for 10 min. The spindle of the rotary viscometer has been immersed into the center of the scaler container (beaker) which contains the paraffin oil and adjusted until the oil level reaches to the groove on the spindle. This process has been followed by setting the machine rotational speed of 30 rpm for 1 min at an ambient temperature of 25°C before reading the measured viscosity. The viscometer apparatus used was Brookfield DV-E Viscometer, USA, with a maximum rotational speed of 100 rpm.

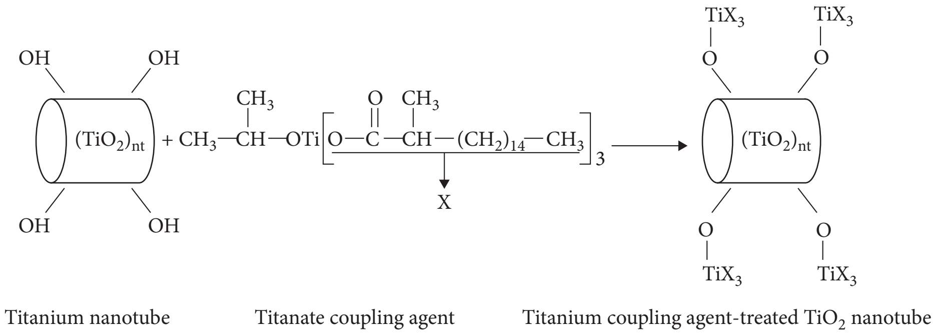


Figure 1: Schematic represents the mechanism of TCA surface treatment on (TiO_2)nt.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR) Test of TiO_2 Nanotubes. The schematic for chemical process of grafting TCA, isopropyl triisostearoyl titanate (KR-TTS), on the surface of titanium nanotube (TiO_2)nt, is shown in Figure 1.

In Figure 1, the hydrolysable group of the isopropyl triisostearoyl titanate (KR-TTS) has been denoted by the (X) letter. However, this hydrolysable group (X) reacted with the hydroxide group (hydrogen and oxygen connected together by a covalent bond and localized on the nanotube (TiO_2)nt surface). Then, it will lead to the creation of the bond that is connecting the Ti(X) of the TCA with the oxygen (O) on the nanotube (TiO_2)nt surface and offering the (O-TiX_3).

Figure 2 represents the FTIR test results of TiO_2 nanotube material before and after treatment with the TCA. The graph area in the figure presenting two spectra, the region before 1,500 cm^{-1} represents the fingerprint of the material itself and the area after the 1,500 cm^{-1} scales represents the functional group region. The wide peak presented in the graph at the fingerprint region for both of the modified TiO_2 (M-TiO_2) and none modified (TiO_2) material and at the range of (400–700) cm^{-1} refers to the Ti–O and O–Ti–O bonds [5, 23–25]. The broad peak presented at 3,320 cm^{-1} and the peak at 1,622 cm^{-1} can be attributed to the bending vibration peak and stretching vibrations peak of the hydroxyl (O–H and H–O–H) available on the surface of TiO_2 nanotube [26, 27]. Upon comparing the graph lines of the treated (M-TiO_2) and none treated TiO_2 nanotube material, the change in peak after treatment presented at 2,381cm^{-1} can be attributed to the stretching vibrations peak initiated from C=O of CO_2, that has been absorbed by the TiO_2 nanotube material [28]. The sharp initiated peak in the line of treated TiO_2 nanotube (M-TiO_2) at 2,919 cm^{-1} represents the absorption peaks of methylene and methyl [29]. Also, at the same modified line b (M-TiO_2) at Figure 2, the small initiated peak at 1,682 cm^{-1} referring to C=O of the titanate coupling agents [25, 28, 30].

However, all of the mentioned factors proof that the functional groups of the coupling agent (isopropyl triisostearoyl titanate (KR-TTS)) have been reacted with the hydroxyl groups available on the surface of the TiO_2 nanotube and caused a change of ceramic surface properties from hydrophilic to be hydrophobic properties.

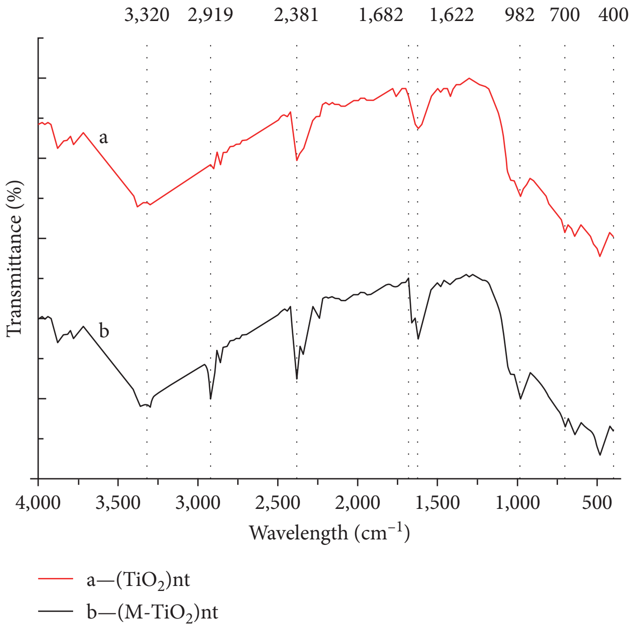


Figure 2: FTIR spectra of a—untreated TiO_2 nanotube and b—titanium-modified TiO_2 nanotube (M-TiO_2).

3.2. X-Ray Diffraction (XRD) Test of TiO_2 Nanotubes. XRD results are presented in the two graph patterns, as shown in Figure 3, it has been indicated a sharp diffraction peaks at 26.1°, 38.48°, 47.43°, 55.67°, 57.6°, and 67.86°, where those peaks represent the anatase crystal phase of the titanate nanotube (TiO_2)nt according to International Center for Diffraction Data (ICDD PDF No. 89–4921) [5, 22, 31].

The XRD figure of the TiO_2 nanotube (TiO_2)nt presents an inconsiderable change in peaks of the modified-TiO_2 curve (M-TiO_2), line b in Figure 3, in comparison to line a in Figure 3 of the nontreated titania nanotubes TiO_2. The only recognizable change is the shifting up of the whole curve, while the overall shape and broad of peaks were almost still the same. The initiated difference was due to the treatment effect of the TCA, while the TCA amount is very small and does not generate any diffraction peaks in the modified-TiO_2 (M-TiO_2), line b in Figure 3, and that means the crystalline structure does not changed upon the modification of TiO_2 nanotube with the TCA.

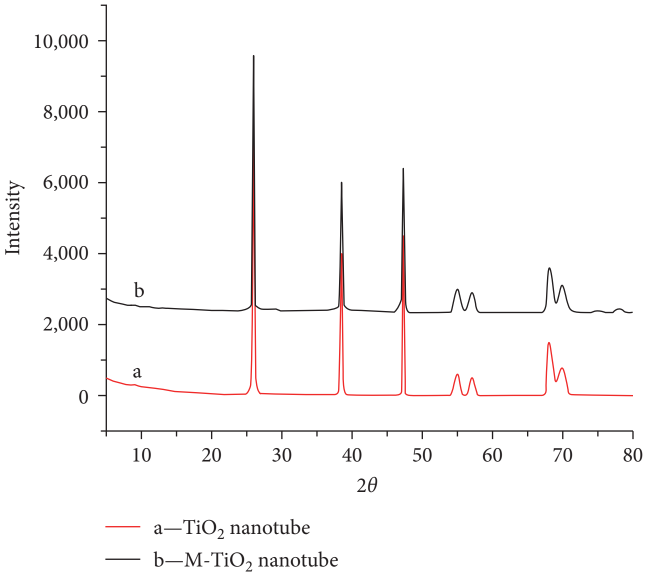


Figure 3: XRD pattern of (a) none treated TiO_2 nanotube (TiO_2) and (b) modified TiO_2 nanotube (M-TiO_2).

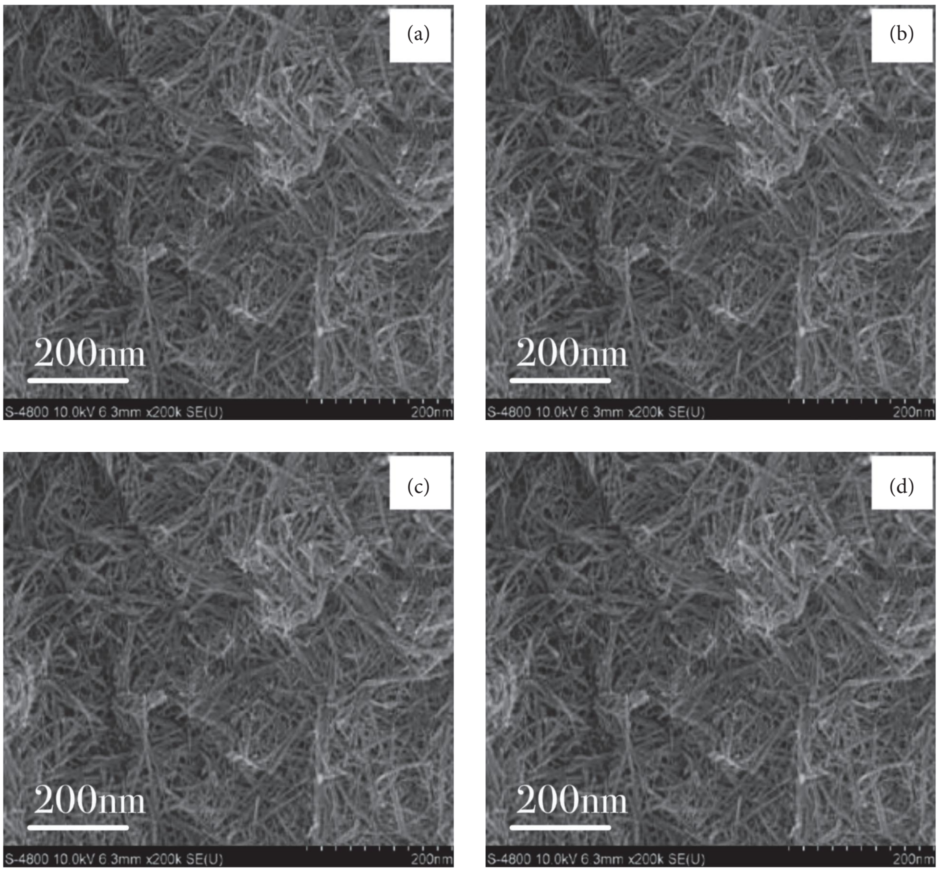
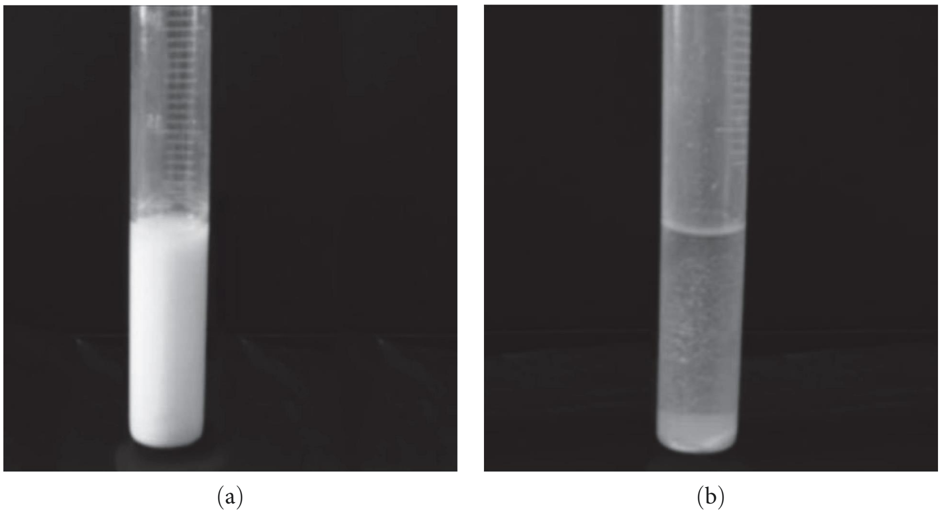


Figure 4: SEM micrograph pictures of (a, b) unmodified TiO_2 nanotubes and (c, d) modified TiO_2 nanotubes.

3.3. SEM Investigation. Figure 4 presents the SEM micrograph pictures for the none modified (TiO_2) nanotubes and modified one (M-TiO_2). Five magnification ranges have been investigated, but only two ranges were selected, 200 and 500 nm deemed suitable for revealing the distribution and agglomeration of nanopowder.

In Figures 4(a) and 4(b), it is clear that a port of unmodified TiO_2 nanotubes has happened to aggregate. While, in



(a) (b)

Figure 5: Dispersion of TiO_2 nanotubes in liquid paraffin for (a) modified (M-TiO_2)nt and (b) nonmodified (TiO_2)nt.

Figures 4(c) and (d), the aggregation of TiO_2 nanotubes is less and weaker. However, according to the SEM micrograph pictures, it could be determined that TCA (isopropyl triisostearoyl titanate (KR-TTS)) works as a perfect compatibility agent for the TiO_2 nanotube and breaking up the aggregation and reduced the agglomeration successfully. Same conclusion has obtained by a study conducted by Monte [32], as it has been stated that the dispersion of inorganic filler, like the $CaCO_3$ and carbon black, will improve and the aggregation will decrease, when the water of hydration available on the particle surface replaced by a monomolecular layer of organofunctional titanate. Similarly, a study carried out by Wah et al. [33] investigating the effect of TCA on the rheological behavior of filling the polypropylene by talc material revealed that TCA had a positive effect in improving the dispersion quality of filler into the matrix material, as well as treatment material causing a decrease in the melt viscosity of the filled polypropylene.

3.4. Viscosity Test. Figure 5 presents the involvement of 10 g from each of modified M-TiO_2 nanotube (test tube a) and nonmodified TiO_2 nanotubes (test tube b) into 150 mL of liquid paraffin. The dispersion of the modified material has been investigated through measuring the viscosity values of immersed TiO_2 nanotubes in liquid paraffin before and after treatment. The obtained results of the measured viscosity of the TiO_2 in liquid paraffine before treatment was 70.30 mPa·s (tube b), as shown in Figure 5, while after modifying TiO_2, as shown in tube a of Figure 5, the measured viscosity decreased to 9.43 mPa·s. That means the viscosity of the modified TiO_2 material in liquid paraffin has been reduced by 86.58%. Also, it can be recognized from Figure 5(a) that the dispersion of the modified TiO_2 (M-TiO_2) in liquid paraffin is uniform, while tube b in Figure 5 presents a precipitation and poor dispersion of unmodified TiO_2 nanotube.

The reason of the high viscosity for the unmodified TiO_2 nanotubes into liquid paraffin was related to the increase of resistance while the spindles rotor of viscometer apparatus flows between two different incompatible materials. However, in the case of M-TiO_2 nanotubes, the dispersion in liquid paraffin was increased and could be related to the change of nanotube surface properties upon treatment. The treatment caused a decrease in resistance which lead to a reduction in the value of viscosity. Therefore, the change in measured viscosities can verify that there was an interaction between the TiO_2 nanotubes and (KR-TTS) TCA and the surface properties of M-TiO_2 nanotubes have been changed from being hydrophilic to be hydrophobic.

4. Conclusion

This study presents the TiO_2 nanotube modification with the TCA of isopropyl triisostearoyl titanate (KR-TTS) type. The chemical investigations conducted by FTIR test verified that the interactions happened between TiO_2 nanotube and some groups of isopropyl triisostearoyl titanate (KR-TTS) have been introduced into the surface of TiO_2-nanotube by coupling reaction with the hydroxyl groups. The XRD structural investigation also confirmed that the crystalline structures of TiO_2 nanotube did not change upon treatment with the TCA (isopropyl triisostearoyl titanate (KR-TTS)). The physical investigations of this study confirmed through the SEM micrographs that the modification process broke up the aggregation of TiO_2 nanotubes into finer particles. Also, the dispersion has been increased in paraffin oil and confirmed through the 86.58% reduction in viscosity measurements of the modified material. However, isopropyl triisostearoyl titanate (KR-TTS) was a perfect treatment material for the modification of TiO_2 nanotube surface and supreme to overcome the agglomeration, improve dispersion, and changing the TiO_2-nanotube materials surface to be of hydrophobic properties.

Data Availability

The graphs and figures data used to support the findings of this study are included within the article. The optimization process results data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors' Contributions

Conceptualization and methodology by B.A.S.; investigation by B.A.S. and M.S.; results analysis by B.A.S., M.S., and A.M.; writing an original draft by B.A.S.; project administration and scientific supervision by M.S and A.M.; methodology, investigation, data curation, and validation by B.A.S.; reviewing and editing by M.S., A.M., C.L.G., and K.R. All authors have read and agreed to the published version of the manuscript as presented.

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