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TiO_2-PDMS Super Hydrophilic Coating with Self-Cleaning and Antimicrobial Properties

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Abstract

In this paper, self-synthesized TiO_2 nanoparticle was used as a coating material with the addition of polydimethylsiloxane (PDMS) on the surface of the glass and ceramic substrate via spray coating. The self-cleaning properties of the coating with photocatalytic activity mechanism were observed under irradiation of black lamp as well as surface wettability. The antimicrobial properties and the morphology under a scanning electron microscope were also investigated. The results showed that the coating exhibited self-cleaning properties, as demonstrated by the photocatalytic degradation of methylene blue up to 80% and wettability as a super hydrophilic layer with a water contact angle less than 10° for both glass and ceramic substrate. The coating also shows an antimicrobial property by extending the radius of microbial growth up to 67% compared to the uncoated sample. 3% TiO_2 addition with 50% w/w PDMS is the optimum coating ratio for maximum photocatalytic activity, super hydrophilic, and antimicrobial properties.

1. Introduction

The use of cleaning chemicals for building maintenance, such as glass and tiles, was reported as more than 25% of the total cleaning product used for household consumption with a worth value of 76.8 million dollars for the Asia Pacific Region [1]. In addition to the expensive cleaning products, building maintenance is also subjected to extensive works and intensive labor as well as significant energy consumption [2]. Coating the building surfaces can be a sustainable method to minimize the use of cleaning chemicals that are not environmentally friendly and a way of reducing the building maintenance cost.

The coating is an additional layer applied to the surface of an object. The purpose of applying the coating may be decorative and functional. Coatings mostly have the objective of protecting the surface from damage or dirt and dust [3]. Another additional function of the coating is that the coating has either self-cleaning or antimicrobial properties. The self-cleaning coating is an additional layer on the surface of an object that in-built the ability to remove any debris or microorganism from their surfaces in various mechanisms. This type of coating is expected to have hydrophilic or hydrophobic wettability properties. Hydrophilic is a mode of material that is attracted to water, while hydrophobic is the opposite. Many components can be used for self-cleaning coating, mainly metal oxides semiconductors such as Al_2O_3, TiO_2, SiO_2, SnO, ZnO, Si_3N_4, MgF_2 [4, 5, 6, 7]. Other research on self-cleaning coating used MnO_2 [8] and the addition of polydimethylsiloxane (PDMS) [9, 10].

TiO_2 nanoparticles have attracted much attention due to their potential application in various products such as catalysts for water treatment systems or renewable energy production, CO_2 reduction, and construction materials. TiO_2 is known for its low cost, good chemical, biological, and thermal stability, and high physical properties and photoactivity [11, 12]. A study revealed that self-cleaning coating using TiO_2 essentially utilizes solar energy to generate electrons and holes used to degrade organic compounds (dirt, dust, oil, and others) [9]. Meanwhile, low surface energy, low reactivity, low toxicity of polydimethylsiloxane (PDMS) are commonly used for structuration and surface modification of a

transparent surface coating [10]. Work on the combination of two materials has been reported that TiO_2 – PDMS provided hydrophobic to superhydrophobic coating with good photocatalytic activity in the decomposition of methylene blue around 70%, rhodamine B 95% with water contact angle above 80-162° [13, 14, 15]. Other research reported combining both materials with other components such as Ag [16] and Si [11] also reported hydrophobic coating with fair photocatalytic activity. In such a manner, the correlation between their wettability and self-cleaning properties as well as antimicrobial properties TiO_2 – PDMS with starch as additional binder needs further investigation. This paper explained a comprehensive work on self-cleaning properties, wettability, antimicrobial properties, and the surface morphology of super hydrophilic TiO_2-PDMS coating on glass and ceramic substrates.

2. Materials and Methods

2.1. Materials

Tetra n-butyl titanate (TNBT) as TiO_2 precursor, Polydimethylsiloxane (PDMS), Polypropylene glycol (PPG) were purchased from Shandong Zhi Shang Chemical Co., Ltd. Other chemicals such as ethanol, isopropyl alcohol, DI water, starch, and potato dextrose agar (PDA) were purchased from the local chemical store CV Indrasari. All chemicals were used without pretreatment.

2.2. Synthesis of TiO_2 nanoparticles

The preparation of TiO_2 nanoparticles as coating-based referred to the methods described in other publications [17]. 200 g TNBT were added into 100 mL ethanol, stirred at 800 rpm for 1 hour at 75°C until the solution transformed into a gel. The gel was then transferred into a furnace for calcination at 500°C for 1 hour. The product was analyzed using XRD and SEM for its crystal structure and morphology. The final product was then used for coating solution.

2.3. Preparation of coating solution

The coating solution was prepared by mixing a proportion of TiO_2 solution, PDMS solution, PPG, and starch. TiO_2 solution was prepared by dispersion of TiO_2 in the ethanol 3:10 ratio (w/v) with continuous stirring for 30 min. After that, 2% PPG was added, and the mixture was then sonicated for 30 minutes with a controlled temperature of 50°C for homogenization. In the meantime, the PDMS solution was prepared by dissolving PDMS resin into isopropyl alcohol with a ratio of 3:10 w/v and continue stirring for 15 minutes. The preparation of 100 mL coating solution was following the ratio variable (v/v) of TiO_2 solution (1,2,3%), PDMS solution (45,50,55%), 1% starch and PPG with continuous stirring for 15 min at room temperature.

2.4. Coating application

Glass and ceramic substrates (50 x 50 mm) were cleaned with DI water and ethanol and dried for 2 hours at room temperature before application. The substrate was then placed in the sample holder vertically, and coating solutions were applied to the surface three times by spray coating with 100 mm distance. After application, the solution was wiped out by wiper and dried at room temperature for 3 hours.

2.5. Coating characterization and analysis

Self-cleaning performance, its organic degradation performance was evaluated by placing five drops (0.5 mL) of 5 ppm methylene blue (MB) in the surface of coated substrate and exposed in the irradiation of black light (Bluelans UV Ultraviolet Fluorescent Blacklight CFL Light Bulb 25W) for 5 hours. Before and after the process, the pictures were taken for RGB analysis using Delphi software for color degradation performance. Photometric analysis was used in the experiment following the procedure described in the literature to measure dye photodegradation rate [18]. First, each sample that contained MB was captured using a digital camera. Then the image was cropped and uploaded in the Delphi software program for each sample's RGB color index value. The calculation of color index parameters R, G, and B is obtained from each pixel in the image. The higher the color index, the brighter the image.

$$I_{blue} = \frac{B}{R+G+B} \quad (1)$$

Wettability, the measurement of surface water contact angle (WCA), was used to determine the surface tendency of the coated sample. The Kruss GmbH contact angle goniometer measured the WCA.

Antimicrobial properties, the performance of self-cleaning coating as protection from bacterial were conducted by exposing the coating solution under the illumination of black light for 2 hours and then use three drops of the solution in the center of media consist of solidified potato dextrose agar. The media contained coating solution was then placed in the incubator chamber for two days for radius microbial growth area.

Surface morphology, *Scanning electron microscopy* (SEM) was used to observe the coated solution's surface morphology. SEM analysis was performed using SEM EDX (Phenom Pro X).

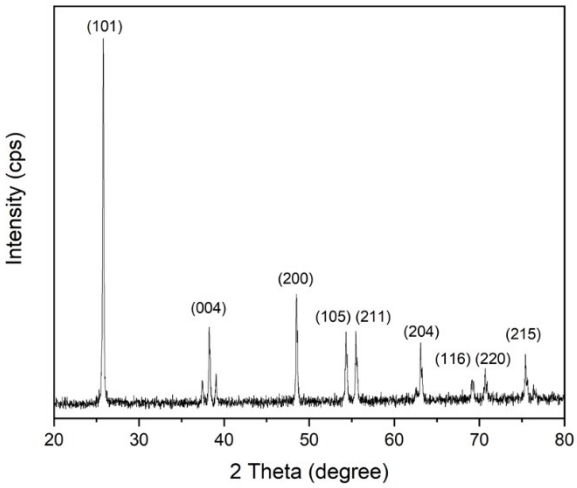
3. Results and Discussion

3.1. Synthesized TiO_2 nanoparticle

The characteristic TiO_2 nanoparticles as coating-based prepared by methods described in other publications can be seen in Figure 1. The XRD pattern shows the peaks at two thetas resemble the pattern of JCPDS card 78-2486, which was the TiO_2 anatase phase. The crystal size of prepared TiO_2 is estimated at approximately 63.5 nm using the Scherrer equation:

$$\tau = \frac{k\lambda}{B(2\theta)\cos\theta} \quad (2)$$

where τ = crystallite size (is the mean size of the ordered (crystalline) domains,); B = peak width (FWHM); θ = Bragg angle; λ = X-ray wavelength; k = Scherrer constant. Meanwhile, the SEM image of the sample shows the very fine particles with sizes less than 100 nm agglomerated within each other.



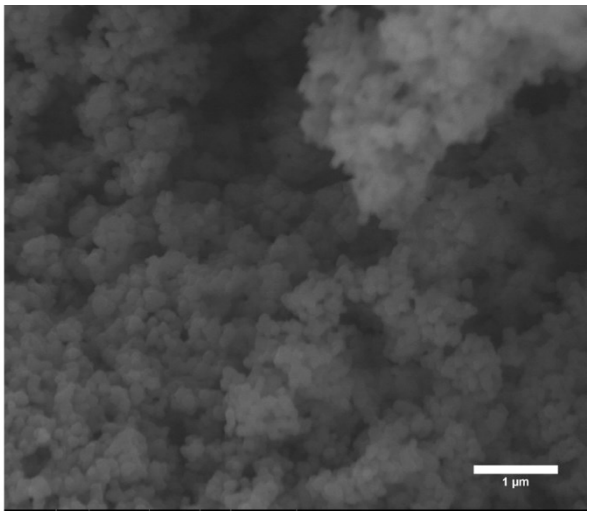


Figure 1. XRD pattern and SEM image of TiO_2 synthesized via sol-gel methods.

3.2. Profile of TiO_2-PDMS coating on organic compound degradation

Self-cleaning properties can be determined by the performance of a surface TiO_2 contained material on organic matter degradation in favor of photon irradiation. Once TiO_2 is illuminated with photons with energy larger than 3,2 eV, the charge excitation will occur and create hydroxyl and oxygen radicals in the environment that consist of H_2O or O_2 and further lead to the reduction and oxidation process. This oxidation and reduction can be translated into organic decomposition into lower-weight molecules with CO_2 and H_2O [12, 19]. In this research, dye (MB) was used as a representative of the organic component.

The profile of TiO_2-PDMS coating on MB degradation can be observed in Figure 2 for the glass substrate and Figure 3 for the ceramic substrate. For glass substrate, the trendline was similar for all PDMS ratio variation, which in other words, the addition of TiO_2 was more obvious in controlling the performance of MB degradation. Even though the percentage were slightly different, as in the addition of 1% TiO_2, the degradation percentage was around 72-74% for PDMS addition (45-55%), or in the addition of 2% TiO_2, the degradation was 75-76% and 77-80% of MB degradation for coating with 3% of TiO_2. However, the degradation was improved gradually by the addition of TiO_2.

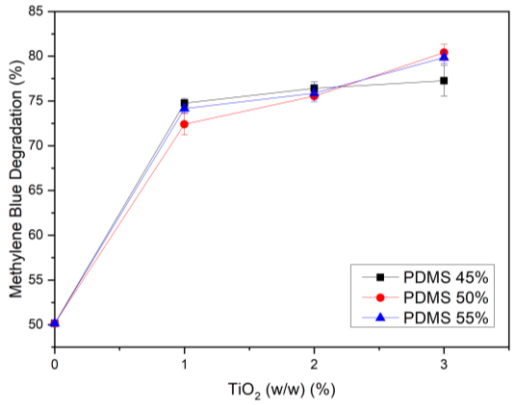


Figure 2. MB degradation of coating with different TiO_2 and PDMS addition on a glass substrate

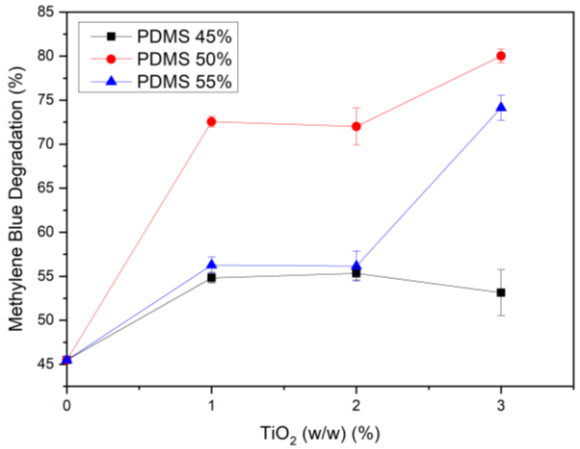


Figure 3. MB degradation of coating with different TiO_2 and PDMS addition on the ceramics substrate

The presence of TiO_2 indeed is the critical factor for optimum organic component degradation. Additional TiO_2 means the more active site of photocatalyst present in the coating solution. It also means that more charges are excited during the photon irradiation, thus generating more hydroxyl radical favored the oxidation and reduction process of organic degradation. TiO_2 was also important in self-cleaning properties on TiO_2-SiO2 hierarchical coating solution [11] and TiO_2–Ag self-cleaning coating for solar panels [16].

TiO_2 semiconductor has an energy band gap of 3.2 eV. If TiO_2 is irradiated with photons that exceeded its bandgap, the electrons (e^-) in the valence band will be excited into the conduction band, and holes will form in the valence band. Hole (h^+) reacts with water producing ·OH while e- reacts with oxygen forming superoxide and reacts further with water producing ·OH, which will degrade methylene blue (MB) as in the following reaction equation [20, 21]:

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^- + h^+) \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + \cdot OH \quad (2)$$

$$h^+ + OH^- \rightarrow \cdot OH \quad (3)$$

$$e^- + O_2 \rightarrow O_2^- \quad (4)$$

$$2O_2^- + 2H_2O \rightarrow 2{\cdot}OH + 2OH^- + O_2 \quad (5)$$

$$\cdot OH + \text{organic compound} \rightarrow \text{intermediate compound} \quad (6)$$

$$2OH\cdot + \text{organic} \rightarrow CO_2 + H2O \quad (7)$$

The different profiles can be seen in TiO_2-PDMS coating on MB degradation ceramic substrate in Figure 3. In this type of substrate, it can be observed that TiO_2 addition is not the only parameter that controls the MB degradation but the synergetic effect of the PDMS addition into the coating solution. Using 50%, PDMS led to the optimum MB degradation by adding 3% TiO_2 80% degradation performance. The difference trendline spotted in the glass and ceramic substrates may be due to the properties of the substrate itself in favoring the photocatalytic process. The photocatalytic process was relying on several parameters, including light intensity and the photon penetration to the surface of the catalyst [12, 20, 21]. Light intensity and photon penetration are closely related to the solution's opacity or the substrate's properties in terms of light absorption. Glass substrate absorbed almost 40% of the light penetration [22]. In contrast, ceramic substrates tend to reflect light [23]. The behavior somehow influences light penetration, thus affect the photocatalysis of the organic degradation [24, 25].

3.3. Surface wettability of TiO_2-PDMS coating

The wettability behavior of TiO_2-PDMS coating is determined by measuring the water contact angle (WCA), which is the angle formed between the surface of the layer and the droplet of the water. Figures 4 and 5 depicted the water contact angle of coating with different TiO_2 and PDMS additions on glass and ceramic substrates. The water contact angle of the glass substrate before the coating was recorded around 96°, and after coating was applied to the surface, the water contact angle was reduced (Figure 4). Surface wettability is classified into superhydrophobic with a water contact angle of more than 150°, hydrophobic with a water contact angle of 90°-150°, hydrophilic with a water contact angle of less than 90°, and super hydrophilic with a water contact angle approaching 0° [26, 27]. The role of TiO_2 in reducing water contact angle is very significant, even though further addition has little effect on the further decrease of water contact angle of the coated glass substrate. By adding 1-3% TiO_2, the water contact angle decreased until 8-9°, which can be classified as a super hydrophilic surface.

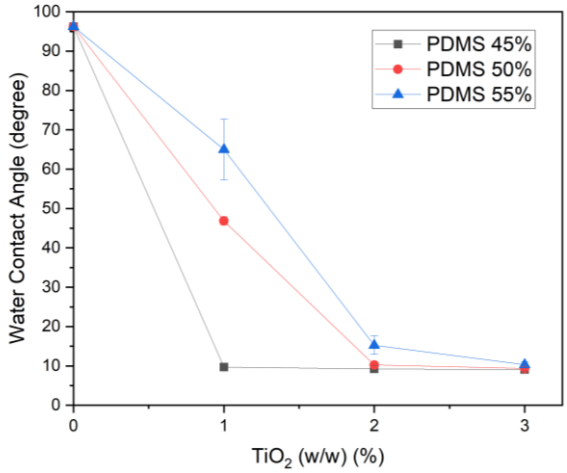


Figure 4. The water contact angle of coating with different TiO_2 and PDMS addition on a glass substrate

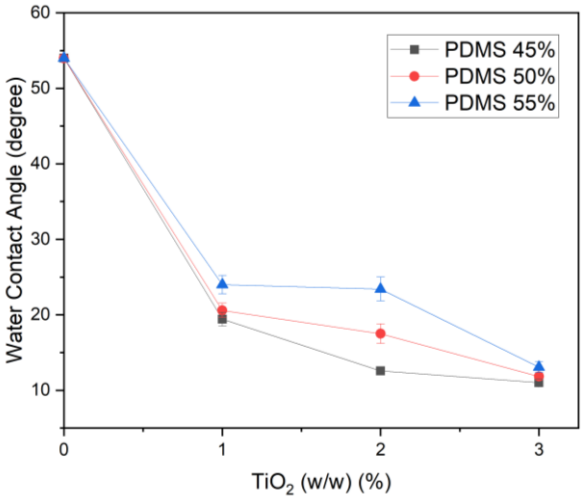


Figure 5. The water contact angle of coating with different TiO_2 and PDMS addition on a ceramic substrate

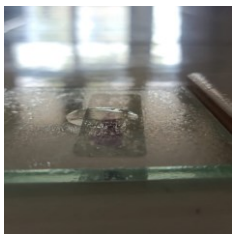
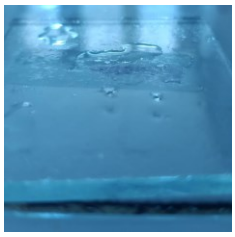
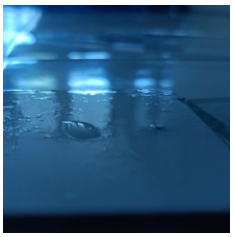
Observing the exact figure, the addition of PDMS inhibits TiO_2 in creating the hydrophilic domains on a coated glass substrate. The nature wettability properties of PDMS are hydrophobic with a water contact angle of 100° [28, 29]. Referring to the opposite nature of PDMS, it is understandable that further addition of PDMS (50-55%) will slowly reduce the rate of hydrophilicity conversion on the surface. Even though eventually, by adding 2-3% TiO_2, the surface completely converted into super hydrophilic.

Figure 5 depicted the initial water contact angle of the ceramic substrate before the coating application was 54° which can already be categorized as a hydrophilic surface [26, 27] and further decreased to 11-13°. The difference between the initial water contact angle of glass and the ceramic substrate is due to the different surface compositions between the two substrates. Glass substrate mainly consists of SiO_2, which has wettability properties in around 90° that are categorized as hydrophobic [30]. Meanwhile, the ceramic substrate consists of various components, mostly CaO and SiO_2, which have wettability properties in around 40-60° [31]. The other theory mentioned the uneven surfaces reduce the surface area of droplets interacting with the layer. As explained by the Cassie-Baxter model, the smaller the surface area of

particles interacting with water, causing large contact angles [31]. In addition, according to the basic assumption of Wenzel's theory is the linear relationship between the angle of surface contact and the surface roughness factor. The smoother the surface, the higher its hydrophilic properties [9].

In ceramic, as shown in Figure 5, the addition of coating consists of TiO_2 leads to a significant decrease in water contact angle. Even after 2-3% addition, the downward was not significant. The tendency is slightly different from the surface in the glass substrate. The PDMS variable apparently was also not significantly affecting the water contact angle as in glass substrate.

Table 1. Water contact angle images before, after coating, and coating with UV irradiation on glass and ceramic substrate

	Glass Substrate	Ceramic
Before coating		
After coating		
After coating with UV radiation		

Earlier research reported the contribution of UV activated TiO_2 to the super hydrophilicity of surfaces such as SiO_2-TiO_2 coating on polycarbonate substrates [32], durable photocatalytic paint contained TiO_2 [33] both reported that the presence of TiO_2 caused a significant decrease in contact angle from 40° to 10° and 162.3° to 75.6° respectively. Others reported the super hydrophilic behavior of TiO_2 coating without ultraviolet-light illumination [34]. Super hydrophilic properties exhibit lower solid/liquid adhesion and a sliding angle smaller than 10°. This phenomenon is due to the generation of high energy fields caused by the excitation of charges that triggered hydrophilic/ oleophilic property on the TiO_2 surface [27]. As data are shown in Table 1, water contact angle images before, after coating and coating with UV irradiation on glass and ceramic substrate, the effect of TiO_2-PDMS coating exhibit a similar tendency to the earlier research, thus confirming the synergetic effect of TiO_2 and PDMS in creating the self-cleaning effect on the surface of the substrate by controlling its water contact angle.

3.4. Antimicrobial performance of TiO_2-PDMS coating

The antimicrobial performance was studied by measuring the radius of average microbial growth from the center of media contained TiO_2-PDMS coating solution. The result of antimicrobial performance can be seen in Figure 6. The radius of average microbial growth from the center media in the sample without TiO_2-PDMS coating solution was 2.25 cm. The sample contains TiO_2-PDMS coating solution the result of radius microbial growth was varied. By adding TiO_2 with constant PDMS composition at 45%, the radius of average microbial growths was increasing steadily from 2.25 to 3.75 cm at 3% TiO_2 addition. On the opposite, by adding more PDMS, the growth of microbes cannot be avoided, and PDMS seems to inhibit the antimicrobial mechanism of TiO_2. The result is also visualized in Figure 7 as it consists of a photograph of microbial growth pictures of control (A) without coating solution and with TiO_2-PDMS coating solution with 1% (B), 2% (C), and 3% (D) of TiO_2 and 45% PDMS.

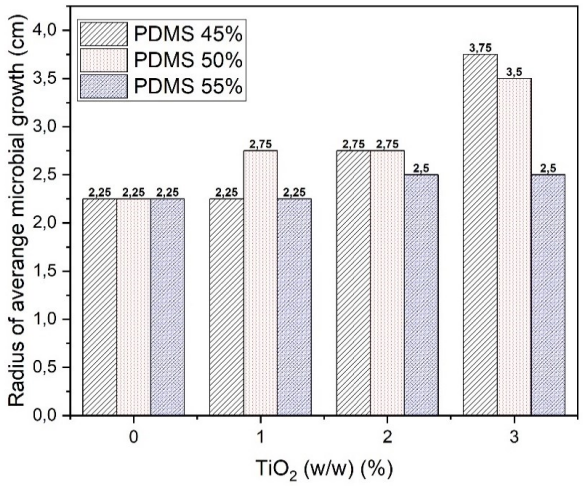


Figure 6. The radius of average microbial growth of coating solution at different ratio TiO_2 and PDMS after UV irradiation

The antimicrobial properties of the TiO_2-PDMS coating solution are primarily related to the photocatalytic effect of TiO_2 after UV irradiation. As mentioned in the previous section, TiO_2 semiconductors tend to excited charges (electrons and holes) once it irradiated by UV light which carries more than 3.2 eV, passing the bandgap energy of TiO_2. Thus the charges triggered the generation of hydroxyl radical and oxygen radical that respond to the destruction of both cell wall and membrane of the microbes causing leakage of intracellular substances [2, 35].

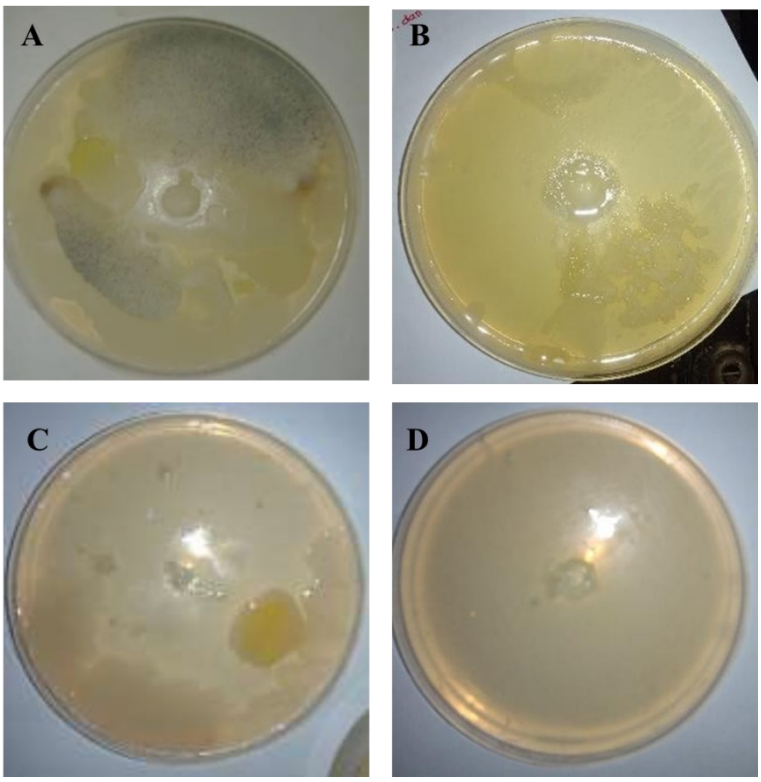


Figure 7. Microbial growth pictures of control (A), coating solution with 1% (B), 2% (C), and 3% (D) of TiO_2 and 45% PDMS

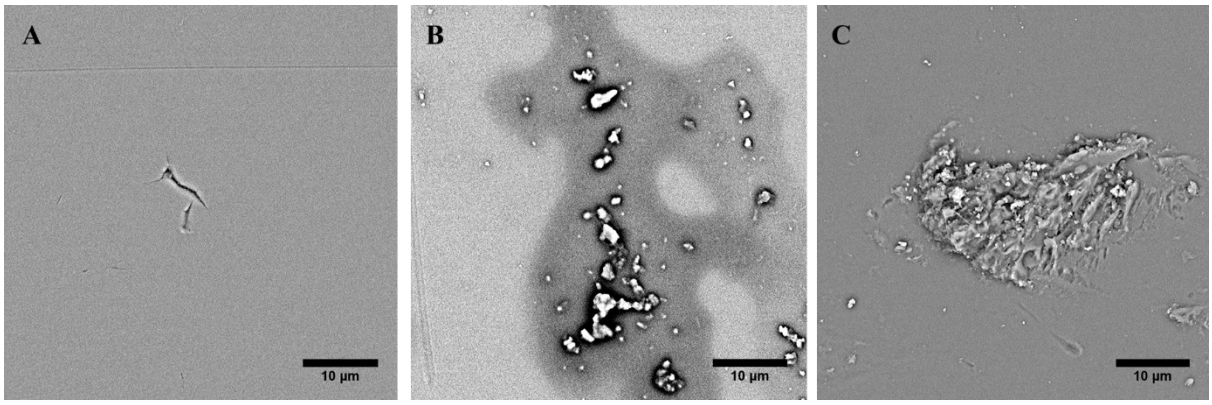


Figure 8. SEM images of glass substrate before coating (A), after coating with 1 and 3% TiO_2 (B, C)

3.5. Morphology of TiO_2-PDMS coating

Morphology of substrate surfaces before and after coating was observed by the image of Scanning electron microscopy (SEM) characterization. Figure 8A shows the clean and smooth surface of the uncoated glass substrate. In contrast, Figures 8B and 8C show the coated glass substrate where uneven particles were spotted in many surface areas, and some of them were clumps and agglomerated in one spot together. TiO_2 used in this study, as mentioned in the previous section, were nanoparticles with a size less than 100 nm. The nature of this type of nanomaterial is that it tends to agglomerate as nanosized particles have high surface energy that led to the agglomeration process as the counter of minimizing the surface energy in the environment [20]. In addition, the agglomeration might happen due to the coating application process, which in this study, the spray coating was used. TiO_2 particles were not evenly distributed throughout the surface and accumulate at the focal point of spraying. After spraying, the solution will flow down slowly from the surface of the substrate so that some TiO_2 particles in the coating solution were accumulated and deposited. The spray coating technique requires a large pressure and speed when firing a solution on a surface to be coated evenly [36].

Figure 8 also confirms the water contact angle result. As mentioned in the previous section, the wettability properties are driven either by the surface energy or the roughness of the surface [9, 10, 27, 31, 37].

4. Conclusion

Nano TiO_2-PDMS coating has been successfully applied on the surface of the glass and ceramic substrate. As the nature of TiO_2 nanoparticle that tends to agglomerate due to high surface energy, thus resulting in the uneven coating within the surface even spray coating with wiping was used as application method. Regardless, the coating still inherits self-cleaning properties proven

by the methylene blue photocatalytic degradation ability up to 80% and wettability as a super hydrophilic layer with water contact angle less than 10° both for glass and ceramic substrate. In addition, the coating also exhibits antimicrobial properties by preventing microbial growth up to 67%. TiO_2 addition 3% and PDMS 50% is the optimum coating ratio for maximum photocatalytic activity, super hydrophilic, and antimicrobial properties.

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