Preparation Titanium Dioxide Combined Hydrophobic Polymer with Photocatalytic Self-Cleaning Properties

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Abstract

Titanium dioxide (TiO₂) and hydrophobic of TiO₂/PDMS (PDMS = polydimethylsiloxane) have been prepared as photocatalytic self-cleaning materials. Synthesis of TiO₂ was carried out using the sol-gel method with titanium(IV) isopropoxide (TTIP) as a precursor and acetic acid as a solvent at a temperature of about 10–15 °C, while the synthesis of hydrophobic of TiO₂/PDMS composites was carried out by a sonication method under ethanol solution. The results of XRD analysis of synthesized TiO₂ showed that TiO₂ was anatase phase. The glass-coated TiO₂/PDMS were prepared by dip-coating under an ultrasonication bath. TiO₂/PDMS composites at a ratio of TiO₂/PDMS (1) on the glass plate showed hydrophobic properties, as evidenced by the contact angle of 104° before irradiation and the contact angle of 99.7° after irradiation. The synthesized titanium dioxide has irregular spherical morphology. The increase in PDMS content was correlated with an increase in the roughness of TiO₂. PDMS not only acts as low surface energy but also binds TiO₂. The hydrophobic behavior of PDMS creates TiO₂/PDMS repel each other, gain irregular agglomeration structures. Beside having optimum contact angle, glass-coated TiO₂/PDMS (1) is the best composition for degradation of methylene blue in 69.68% for 20 minutes irradiation. Copyright © 2020 BCRec Group. All rights reserved

Keywords: Self-cleaning; Photocatalytic; Sol-gel; TiO₂/PDMS; methylene blue

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1. Introduction

Nowadays, thin-film outer layer on products as doors and windows need self-cleaning glazing. Knowledge about cleanliness, withstand contaminating, and performance over time is of excellent importance. We need a scientific method to quantify the self-cleaning effect by choosing a self-cleaning glazing product in preference to a regular product, then considering the actual profit.

In 1997, self-cleaning based on easy-to-clean coatings has been widely used in the surface field using superhydrophilic and photocatalytic materials [1]. Photoinduced super hydrophilicity of titanium dioxide (TiO₂) films are commercially applicable for self-cleaning
properties were purpose by using composite systems or only pure of TiO$_2$ [2]. Many kinds of self-cleaning nanocoating materials deposited on the surface of any kind of common glass are based on the photocatalytic property of a thin layer of titanium dioxide (TiO$_2$) nanoparticles.

The superhydrophobic surfaces have low free energy surfaces. The developed self-cleaning utilizes the superhydrophobic surface and the photocatalytic properties of materials [2]. Superhydrophobic materials with a water contact angle (WCA) higher than 150° causing water droplets can thus easily roll across the contaminant from the glass substrate [3]. The hydrophobic surfaces are as usual designed through the controlling of the morphology of solid surfaces and chemical compositions [4].

Superhydrophobic polymers, such as PDMS, is widely used because they have high elasticity, environmentally friendly, chemical inertness, and low cost [5–8]. PDMS has a nonpolar group like –CH$_3$—that makes the ability of contact with pollutants, such as: dye and nonpolar group [9]. PDMS has excellent durability and mechanical properties is a stable cross-linked structure, so easy to use with the composition of materials [3].

On the other hand, the advantages of TiO$_2$ are high chemical stability for base-acid, non-toxic, low cost, and high photo-reactivity [10]. The TiO$_2$ have synthesized by sol-gel [11], solvothermal [12], thermal plasma [13], and others. The highest photocatalytic performance of TiO$_2$ is the anatase phase compared with the brookite and rutile phase [11–13].

The combination between TiO$_2$ as photocatalyst and PDMS as hydrophobic polymer generates stability of self-cleaning properties [14]. Fabricating a hydrophobic-hydrophilic multifunctional surface coating is demonstrated by blending various PDMS and TiO$_2$ nanoparticles. After coating, various blend solutions onto a substrate dried at 110 °C. The surface of –CH$_3$ was obtained through the combined contributions of aggregated TiO$_2$ nanoparticles and hydrophobicity properties are contributed by PDMS as the low surface energy [3].

Fabrication of TiO$_2$/PDMS creates superhydrophobic surfaces. The photocatalytic properties of TiO$_2$ make them possible to work in harsh environmental conditions. When exposing to high-energy ultraviolet light irradiation, electron and holes of TiO$_2$ are generated to form free radicals, that can decompose organic pollutants [14]. The self-cleaning glazing needs a hydrophobic surface when a TiO$_2$-based hydrophobic surface is polluted by contaminants. The TiO$_2$ can degrade the contaminant and recover the hydrophobic properties. However, the TiO$_2$ will also degrade those low surface energy materials that constitute the hydrophobic films, resulting in extremely poor durability which represents a hurdle to be controlled. So, the combination of TiO$_2$ and PDMS needs to be provided.

Tavares et al. [15] have reported TiO$_2$/PDMS composite for self-cleaning was processed by spray coating and TiO$_2$ was synthesis by high temperature on microwave-assisted hydrothermal. The composite prepared use hexane solution. In 2020, Julian et al. [16] research PDMS-coating TiO$_2$ using vinyl and hydroxyl-terminated polydimethylsiloxane for functionalization of TiO$_2$. However, these methods need to be improved with the adding of TEOS that can prevent the TiO$_2$/PDMS from cracking during drying.

In this work, we focus on preparing composite photocatalytic-hydrophobic TiO$_2$/PDMS coated on the glass substrate for decolorization of methylene blue. The composite TiO$_2$/PDMS using TEOS as silane and ethanol coated on glass substrate were fabricated using the dip-coating technique under the ultrasonicator bath. Before preparation on glass substrate, we focus to produce the anatase phase of TiO$_2$ by a gel-sol method using a weak acid solution. The ability of self-cleaning TiO$_2$/PDMS was evaluated by measuring the water contact angle (WCA) and decolorization of methylene blue.

2. Materials and Method

2.1 Materials

Ethanol absolute 96% was bought from Merck, Titanium(IV) isopropoxide (TTIP) from Sigma Aldrich (CAS No. 546-68-9), Tetraethyl orthosilicate (TEOS) (CAS No. 78-10-4), aquadest, acetone (CAS No. 67-64-1), polydimethylsiloxane (PDMS), acetic acid glacial, methylene blue was purchased by PUDAK Scientific (CAS No. 61-73-4).

2.2 Fabrication of Hydrophobic Polymer

2.2.1 Synthesis of TiO$_2$

A 10 mL TTIP was added into 100 mL acetic acid glacial in a distilled water bath (15 °C) and continually stirred with heat up to 90 °C using hot plate Thermo SP131320-33 Q until a white solution was obtained. The prepared precipitates were freeze and followed by heated up
to 150 °C for 24 hours. After being washed with ethanol and dried for 3 hours at 100 °C, a white powder was obtained. Finally, the prepared powder was annealed at a temperature of 400 °C for 2 h at a 10 °C/min heating rate.

2.2.2 Preparation of TiO$_2$/PDMS

Preparation of TiO$_2$/PDMS composite by modifying a method reported previously [17]. 10 mg TiO$_2$ was added into PDMS in 200 mL ethanol and then sonicated at 25 °C for 30 minutes (Figure 1). The TiO$_2$/PDMS materials have been prepared by variation of TiO$_2$ and PDMS amount as shown in Table 1.

2.2.3 Preparation of the glass substrate

Glass substrate with 7 cm × 3 cm × 0.3 cm cleaned to remove organic or non-organic pollutant. Glass substrate put into beaker glass with aquadest and ultrasonicated for 10 min and then oven on 100 °C for 10 min. After that, ultrasonicated in ethanol and acetone solution alternately by the same time and temperature. The glass was dip-coated in various composition composite hydrophobic TiO$_2$/PDMS, ultrasonicated for 30 min on 25 °C (with four repetitions). Glass was heated for 110 °C for 30 min. Hydrophobicity TiO$_2$/PDMS coating on the glass. The measurement of the contact angle by drop the water on the glass surface.

2.2.4 Photocatalytic Self-Cleaning properties

Photocatalytic self-cleaning of glass substrate coating was evaluated by methylene blue degradation. 5 mL methylene blue 10 ppm was dropped on glass coated TiO$_2$/PDMS and irradiated with halogen lamp by photon energy source in a closed reactor for 20 min with 5 min increment. After that, methylene blue was poured into a beaker glass and then poured into a cuvet for analysis. Degradation of methylene blue was analyzed by spectrophotometer UV-Vis at the range of 500–700 nm.

2.3 Characterization

Characterization of TiO$_2$ by XRD (Shimadzu XRD-600) with Cu-K$_\alpha$ (λ=1.5418 Å), operated at 40 kV and 30 mA (range 20 = 5–80°) to the identification of crystallinity and crystal phase. Morphology and element composition of TiO$_2$/PDMS coating on glass substrate were identified by SEM (FE Inspect-S50). Function group were characterized by FTIR (Fourier Transform Infrared Spectroscopy Prestige 21 model 8201 PC). Degradation of methylene blue was determined by UV Vis Spectrophotometer (Shimadzu UV-2550) with range wavelength is 500–700 nm. The contact angle was taken using a modification WCA box (10 × 25 cm) by Bengkel Bubut Utama (local market), then measured by ImageJ software.

3. Result and Discussion

3.1 XRD Characterization

The reaction of TiO$_2$ synthesis with titanium(IV) isopropoxide (TTIP) precursors is occurred as follows:

\[
\text{Ti(iPr)$_4$} + \text{CH$_3$COOH} \rightarrow \text{Suspension TiO$_2$} \\
\text{Suspension TiO$_2$} \rightarrow \text{Sol-gel TiO$_2$} \\
\text{Sol-gel TiO$_2$} \rightarrow \text{Xerogel TiO$_2$} \\
\text{Xerogel TiO$_2$} \rightarrow \text{Powder TiO$_2$ (anatase)}
\]

| Materials | TiO$_2$ (mg) | PDMS (mg) | TEOS (mg) | Ethanol (mL) |
|-----------|--------------|-----------|-----------|--------------|
| (1)       | 10           | 90        | 0         | 200          |
| (2)       | 10           | 85        | 5         | 200          |
| (3)       | 10           | 80        | 10        | 200          |
| (4)       | 10           | 75        | 15        | 200          |
| (5)       | 10           | 70        | 20        | 200          |

Figure 1. Illustration of preparation of TiO$_2$/PDMS composite.
The sol-gel process was formed by hydrolysis reaction and polymerization process. Figure 2 shows the XRD patterns of TiO₂ crystallizes in anatase phase and the structure confirm to JCPDS No. 78-2486. The diffractogram peaks representing TiO₂ are shown at \( \theta = 25.333^\circ \) \( (d_{101} = 3.513\text{Å}) \), \( \theta = 37.79^\circ \) \( (d_{004} = 2.3784 \text{Å}) \); \( \theta = 48^\circ \) \( (d_{200} = 1.8937 \text{Å}) \), \( \theta = 54.32^\circ \) \( (d_{105} = 1.6875 \text{Å}) \), \( \theta = 62.83^\circ \) \( (d_{211} = 1.4778 \text{Å}) \). The formation of anatase TiO₂ crystal phase has a higher photocatalytic activity than other crystal phases [18].

The TiO₂ as synthesized from the hydrolysis of TTIP in acetic acid glacial (acidic solution) and the calcinated at 400 °C shows that it has low crystallinity. Since the synthesis process, peptization in the sol-gel method influences the crystallinity. The calcination temperature affects the crystallinity, at a temperature of 400 °C the amorphous obtained was according to Mahshid et al. [19]. However, high calcination temperature can transform anatase to rutile phase.

In a previous study, on annealing result of TiO₂ prepared at 500 °C, the rutile TiO₂ was found with a peak at \( \theta = 27.50^\circ \) \( (d_{110} = 3.2394 \text{Å}) \), and we have founded more rutile peak at TiO₂ annealed at 600 °C and 700 °C, respectively. Some of the anatase peaks of TiO₂ disappear, while the peak represented as a rutile TiO₂ was increased [20].

3.2 Scanning Electron Microscope (SEM)

The scanning electron microscope was used for identified the morphology of TiO₂/PDMS composite. The modification mechanism reaction during the synthesis process as shown in Scheme 1. Polydimethylsiloxane binds to

![Figure 2. X-ray Diffraction spectra of TiO₂.](image)

Scheme 1. Reaction mechanism of TiO₂/PDMS composite coating on the glass substrate.
TiO₂ surface with TEOS as a bridge. On the surface of TiO₂, oxygen (electronegative) was bind to silicon which derives from TEOS. The morphology of TiO₂/PDMS was identified in Figure 3. It shows that the morphology of TiO₂ is irregular spheres. The addition of PDMS produces microscale surface roughness which caused by the aggregation of TiO₂ particles. The PDMS matrix is bound together with TiO₂ particle agglomeration, as was the case in previous studies [8]. There are many bumps that indicated that an increase of PDMS can be wrapped up TiO₂.

3.3 Fourier Transform Infra Red (FTIR)

The FTIR spectra of TiO₂ and TiO₂/PDMS composites is depicted in Figure 4. The Si(IV) and Ti(IV) metal alkoxides are reported to show absorption bands associated with stretching modes ν(M–O) of about 800 and 620 cm⁻¹ [21]. Strong peaks of PDMS at 800 and 1264 cm⁻¹ were associated with CH₃ deformation and CH₃ asymmetric bending vibrations [21].

With respect to hydrolysis and condensation, peaks at 900 and 1096 cm⁻¹ indicate a shortening of the Si–O bond distance, an average reduction of Si–O–Si, and bond angles of Si–O–Ti. Near peaks with low frequency at 450 cm⁻¹ indicate Si–O–Si from the bending plane. Peaks at 790 cm⁻¹ and 1050 cm⁻¹ are ascribed to symmetrical stretching and Si–O antisymmetric vibrations according previous study [21]. At the peak range of

![Figure 4. FTIR spectra of TiO₂ and TiO₂/PDMS composite.](image4.png)

![Figure 3. Micrograph of (a) TiO₂, (b)-(f) TiO₂/PDMS composites.](image3.png)
900–1000 cm\(^{-1}\), it is reported of Si–OH, Ti–OH, and Si–O–Ti [21]. The peak at 1255–1266 cm\(^{-1}\) is symmetrical CH\(_3\) vibration from PDMS (Si–CH\(_3\)) [9] and the peak of CH from –CH\(_2\)/CH\(_3\) was detected in 2958–2968 cm\(^{-1}\) [21].

3.4 Hydrophobic-Hydrophilic Properties

The contact angles of glass coating before and after irradiation shown in Figure 5. Based on the measurement, the contact angle of the glass before and after coating by TiO\(_2\) is 59.8° and 81.56° shows that coating influence the contact angle. These hydrophobic-hydrophilic properties can be used as self-cleaning agents. Identification as a hydrophobic material is due to it produces water contact angles \(\theta > 90^\circ\) and to be hydrophilic, because it produces contact angles water \(0^\circ < \theta < 90^\circ\) [22].

Water droplets on the surface of the glass substrate coating with TiO\(_2\)/PDMS form a circle with a high contact angle. Along with the decrease in the compositions of hydrophobic polymers composite (TiO\(_2\)/PDMS) and the increase in the composition of TEOS, it causes the contact angle of droplets are lower (Figure 6 and Figure S1).

The composition of TiO\(_2\)/PDMS (1) deposition on the glass shows the highest contact angle of 104°, because the presence of the CH\(_3\) group (methyl group) in PDMS increases the hydrophobicity properties which is in accordance with the results of previous research [9]. After light irradiation on the glass-coated TiO\(_2\)/PDMS (1), the contact angle decreased to 99.7° indicating the occurrence of the photocatalytic process.

3.5 Photocatalytic Activity of Glass Coated TiO\(_2\)/PDMS using Methylene Blue

The application of photocatalytic as a self-cleaning material works based on the principle

![Figure 5](image_url)

**Figure 5.** The contact angle before irradiation a) glass; b) glass with TiO\(_2\) coating; and after irradiation c) glass; d) glass with TiO\(_2\) coating.

![Figure 6](image_url)

**Figure 6.** The glass/TiO\(_2\)/PDMS contact angle measurement, before and after irradiation.
of photocatalytic reactions on the substrate coating of TiO₂. After the TiO₂ absorbs the UV light as a photon source, the electron/hole (e⁻/h⁺) was formed. Electron was excited to conduction band, while hole (h⁺) are on valence band. Electrons and holes are recombined, but small amounts of them react with O₂ electron acceptors and with electron donors OH⁻ and H₂O to form •O₂ and •OH. These radicals, as detoxifying agents, degrade methylene blue dyes. Detoxifying agents (•O₂ and •OH) will break down the methylene blue into environmentally friendly compounds. The photodegradation mechanism of methylene blue is occurred when the •OH group attacks the C=S=C. The degradation of methylene blue produces CO₂, SO₂, NO₂, and H₂O which are not harmful to the environment [23–24].

The photocatalytic self-cleaning activity test of glass coated TiO₂/PDMS with time variations shown in Figure 7 (Figure S2) and the percentage of degradation shown in Table 2. The best degradation of methylene blue with degradation reached 69.68% occurred in TiO₂/PDMS composite synthesized from TiO₂/PDMS (1)= 1.90 mg. This is because TiO₂ and PDMS are physically bonded. Light irradiation direct to TiO₂ leads to optimum hydroxyl radical production, because TiO₂ was not a big deterrent to photon exposure. Direct light irradiation to TiO₂ causes optimal hydroxyl radical production. However, the resistance of surface bonding and the hydrophobic properties of the PDMS in the composites are also other considerations that need to be considered.

Self-cleaning of methylene blue on a glass substrate coated with TiO₂/PDMS occurs by after exposure to visible light releases electrons into the conduction band which results in e⁻cb and holes (h⁺) in the valence band. then e⁻cb will react with O₂ to produce •O₂⁻. Reaction of O₂ radical production is as follows [25]:

\[ e^{-}_{cb} + O_{2} (ads) \rightarrow •O_{2}^{-} \]

![Figure 7. Methylene Blue degradation by glass coated TiO₂/PDMS (1-5) composite variations (a) Plots of A/A₀ versus irradiation times and (b) Photocatalytic degradation profiles of methylene blue (TiO₂/PDMS (1))](image)

**Table 2.** Methylene blue degradation by TiO₂/PDMS composites coating on the glass substrate.

| TiO₂/PDMS Composites | Methylene Blue Degradation (%) |
|-----------------------|--------------------------------|
|                       | 5 min  | 10 min  | 15 min  | 20 min  |
| TiO₂/PDMS (1)         | 19.87  | 32.47   | 48.68   | 69.68   |
| TiO₂/PDMS (2)         | 8.23   | 10.18   | 38.59   | 56.24   |
| TiO₂/PDMS (3)         | 25.64  | 37.11   | 37.89   | 42.4    |
| TiO₂/PDMS (4)         | 14.72  | 15.06   | 23.47   | 30.55   |
| TiO₂/PDMS (5)         | 4.97   | 22.02   | 9.53    | 9.12    |
$h^+$ will react with $\text{H}_2\text{O}$ to produce $\text{OH}$ that adsorbs monolayer on surface of TiO$_2$ with reaction following:

$$\text{H}_2\text{O} + h^+ \rightarrow \cdot \text{OH} + \text{H}^+$$

$$\text{H}^+ + e^- \rightarrow \cdot \text{H}$$

$$2\cdot \text{H} + \text{O}_2 \rightarrow 2\cdot \text{OH}$$

$\cdot \text{O}_2^{-}$ decomposes methylene blue by reduction process, while $\cdot \text{OH}$ was decomposed by oxidation. The absorbance of methylene blue decreases with increasing irradiation time. These results indicate that the longer time of irradiation can make more electrons are excited whereas electrons take effect of photodegradation self-cleaning activity.

4. Conclusion

We have successfully synthesis TiO$_2$/PDMS composites to coat in a glass substrate under a ultrasonication bath. The TiO$_2$/PDMS (1) composite on the glass substrate produces stability of self-cleaning properties materials, that are hydrophobic properties with contact angle 104° and characteristic for self-cleaning photocatalytic for degradation of methylene blue under visible light irradiation in 69.68%. Therefore, the TiO$_2$/PDMS composites is possible as candidates for coating materials to apply in the glass substrate for glass self-cleaning technology.

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Appendices (Supporting Information)

**Figure S1.** The contact angle Glass/TiO$_2$/PDMS before light irradiation a-e) variation 1-5 and after light irradiation f-j) variation 1-5
Figure S2. Photocatalytic degradation profiles of methylene blue by glass coated TiO$_2$/PDMS (1-5) composite variation