PREPARATION COMPOSITE TiO$_2$ ANATASE WITH POLYDIMETILSILIOXANE AND POLYTETRAFLUROETHYLENE FOR SELF CLEANING ON GLASS SUBSTRATE

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Abstract. Synthesis of TiO$_2$-PDMS and TiO$_2$-PTFE composites were carried out. Preparation of TiO$_2$ used ball milling technique. This study aims to determine the effect of adding PDMS and PTFE to the self-cleaning activity of TiO$_2$, which can be measured by determining the change in contact angle and photocatalytic character of TiO$_2$. The photocatalytic-based self-cleaning character was determined by Rhodamin B degradation.. The results showed the characteristic peaks of TiO$_2$ anatase in (20) = 25.39º; 37.781º; 48.07º; 54.10º; dan 62.902º. The existence of PDMS and PTFE is supported by the results of FTIR analysis that appear absorption at wavelengths around 795 cm$^{-1}$ - 1265 cm$^{-1}$ for PDMS, 1154 cm$^{-1}$ and 1212 cm$^{-1}$ for PTFE. In addition, it is also supported by AFM imaging results that show the roughness of the TiO$_2$-PDMS and TiO$_2$-PTFE composites. The Results of contact angles measurement from glass/TiO$_2$-PDMS is 133,47º and after being irradiated is 27,13º. The Results of contact angles measurement from glass/TiO$_2$-PTFE is 117,37º and after being irradiated is 34,70º. The highest degradation of Rhodamin B was 37.04% for glass/TiO$_2$-PDMS and 47.67% for glass/TiO$_2$-PTFE which is produced in the self-cleaning process for 20 minutes.

1. Introduction

Glass is a transparent material that is often used in buildings today. Glass has a variety of practical uses in various fields of industry, building construction, automotive, and others [1]. Glass can also adorn property and can be used to save energy. The increasing use of glass in buildings, especially in skyscrapers, creates another problem. The problem comes from how to clean it. If cleaning is done manually with human labor it can be risky. Various strategies have been used to modify the glass, one of which is self-cleaning technology [2].

Self-cleaning technology works by utilizing the photocatalytic effect produced from a chemical compound so that it can clean the glass substrate from impurities. Self-cleaning has two stages based on its nature in dealing with water. The surface of the glass can be hydrophobic or hydrophilic [3]. Materials that have self-cleaning properties are very useful for helping human work and have simple cleaning methods [4].

Titanium dioxide (TiO$_2$) can be applied in the fields of photocatalysts, solar cells, anti-fungal, antibacterial, antifungal, paint protective coatings, and wastewater cleaners. Application of TiO$_2$ in daily life can be used because TiO$_2$ is non-toxic, has high chemical stability, and high photocatalytic reactivity and is inert. To improve photo activity and photocatalytic efficiency of TiO$_2$ can be done by modifying the material. This modification can be done by doping the surface of TiO$_2$. The doping can be carried out using hydrophobic material. Polydimethylsiloxane (PDMS) and polytetrafluoroethylene (PTFE) are hydrophobic materials. In addition PDMS and PTFE also have other advantages that can absorb light in the ultraviolet and visible light, have inter-layer force with a substrate that is strong enough, low surface energy, and are a hydrophobic coating polymers that has good stability in acidic or basic environments. Increased photoactivity on TiO$_2$ will improve the self-cleaning process as indicated by the increased ability to respond to visible light. Composite self-cleaning activity was
tested by degradation of rhodamine B dyes which were known from a decrease in dye concentration based on UV-Vis absorbance.

Conducted a study of photocatalytic activity, in which the coating was synthesized by the spray coating method using TiO$_2$ which was added with PDMS [5]. From the results of these studies obtained contact angles above 80° and after being irradiated with UV light the contact angles turned to hydrophilic. Kamegawa et al also conducted research on photocatalytic activity, where layers were synthesized using TiO$_2$ added with PTFE [6]. From the results of these studies obtained a contact angle of about 120° and after being illuminated with UV light the contact angle changes to hydrophilic.

2. Experimental
2.1. Preparation of TiO$_2$

TiO$_2$ preparation using the ball mill method refers to the method of Fadillah et al [7]. TiO$_2$ is ball milled with a ball ratio: TiO$_2$ = 20: 1 and the rotating speed is set at 1000 rpm for 4 hours. Ball-Milled TiO$_2$ were dissolved in 8 N NaOH then refluxed for 24 hours at 120 °C. The solution was neutralized with 2M HCl then filtered and dried at 60 °C for 12 hours and calcined at 400 °C for 2 hours. The dry precipitate was then characterized using XRD, FTIR and SEM.

2.2. Preparation of TiO$_2$-PDMS and TiO$_2$-PTFE composites

10 mg of TiO$_2$ ball milled was added to 70 mg, 75 mg, 80 mg, 85 mg, and 90 mg of PDMS or PTFE in 200 mL ethanol. Then TEOS was added with variations 0 mg, 5 mg, 10 mg, 15 mg, and 20 mg (Table 1). Characterization was carried out using FTIR and SEM.

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

2.3. Glass Substrate Preparation

Glass with a size of 7 cm x 3 cm x 0.3 cm is cleaned to remove organic or inorganic impurities that stick [8]. Glass substrate is inserted into a beaker containing acetone and then vibrated with an ultrasonic cleaner for 15 minutes. Then the washed glass is dried at 100 °C for 10 minutes. The washing process is continued with ethanol and distilled water alternately with the same time [9].

2.4. Deposition to Glass Substrate

Deposition to the glass substrate is done by the dip coating method. The synthesized TiO$_2$-PDMS and TiO$_2$-PTFE composites were respectively dissolved in 200 mL ethanol. Glass is inserted in the beaker containing the solution with a variety of compositions of TiO$_2$-PDMS and TiO$_2$-PTFE composites. The beaker that has been filled with glass and composites is sonicated with an ultrasonic cleaner for 30 minutes at a temperature of 25 °C and is repeated 4 times. Then the glass is heated at 110 °C for 30 minutes. The test is done by measuring the contact angle and with the Rhodamin B degradation test using a UV-Vis spectrophotometer.
2.5. Self Cleaning Activity test on Glass Substrate

2.5.1 Hydrophobicity of TiO$_2$-PDMS and TiO$_2$-PTFE Coated Glass

The hydrophobic properties of the coated glass were tested by measuring the contact angle. Contact angle measurement is done by dripping a dye (Rhodamin B) on the surface of the coated glass and then being photographed. The contact angle is measured using software image J.

2.5.2 Photodegradation of Rhodamin B

5 mL of 10 ppm rhodamine B dye was dripped on TiO$_2$-PDMS and TiO$_2$-PTFE coated glass. The glass was irradiated for 5, 10, 15, and 20 minutes later the degradation results were characterized using a UV-Vis spectrophotometer.

3. Results and Discussions

The preparation of TiO$_2$ material refers to research conducted by Fadillah et al [7] through a ball mill process with a speed of 1000 rpm for 4 hours. The results of TiO$_2$ ball milled were analyzed by X-ray diffraction using Cu Kα radiation (λ = 1.5406 Å). The peak obtained from the measurement results by XRD is matched with X-ray diffraction standards, namely the JCPDS (Joint Committee on Powder Diffraction Standards) [10].

The diffraction pattern of TiO$_2$ can be shown in Figure 1. The diffractogram shows that TiO$_2$ has a dominant peak at (2θ) = 25.39° (d$_{101}$=114.37 nm), (2θ) = 37.78° (d$_{004}$=76.33 nm), (2θ) = 48.07° (d$_{200}$=111.23 nm), (2θ) = 54.10° (d$_{105}$=122.19 nm), dan (2θ) = 62.90° (d$_{211}$= 90.41 nm). These results are areas of anatase phase TiO$_2$ characterization in accordance with JCPDS No. 21-1272.

![Figure 1. X-Ray Diffractogram of TiO$_2$.](image)

Preparation of TiO$_2$-PDMS and TiO$_2$-PTFE were carried out by sonication method. PDMS and PTFE are used as dopants because PDMS and PTFE have hydrophobic and transparent surfaces. PDMS and PTFE are polymer materials with low surface energy, thus causing PDMS to have hydrophobic properties. The PDMS or PTFE material binds to the TiO$_2$ surface bridged by TEOS by means of which three ethyl groups from TEOS will break away so that the three O atoms can bind to TiO$_2$. TiO$_2$-PDMS composites were tested by infrared spectroscopy (FTIR) to determine the bonds
formed. Based on the TiO$_2$-PDMS FTIR spectra shown in Figure 2a, the existence of TiO$_2$ can be seen in wave numbers 1154 cm$^{-1}$ and 1214 cm$^{-1}$ which indicate the presence of Ti-O bonds. Absorbance at wave numbers 1096 cm$^{-1}$ and 1021 cm$^{-1}$ indicates the presence of Si-O-Si bonds. Whereas the wave number 2964 cm$^{-1}$ indicates the presence of CH$_3$. The presence of Si-CH$_3$ bonds originating from PDMS can be seen from the absorption at wavelengths of 800 cm$^{-1}$ and 1262 cm$^{-1}$. Based on the TiO$_2$-PTFE FTIR spectra shown in Figure 2b, the existence of TiO$_2$ can be seen in wave numbers 1154 cm$^{-1}$ and 1214 cm$^{-1}$ which indicate the presence of Ti-O bonds. While the presence of PTFE can be seen at wave numbers 1154 cm$^{-1}$ and 1212 cm$^{-1}$.

**Figure 2.** FTIR spectra of composites (A = TiO$_2$-PDMS, B = TiO$_2$-PTFE).

Composite coating on glass substrate using dip coating method then analyzed using AFM. The results of the 3-dimensional analysis are shown in Fig. 3 and the roughness measurements are shown in Table 2. Analytical techniques using AFM following surface morphology have been proven to be very flexible and powerful tools for surface imaging at nanometers to submicrometer level and the revelation of surface characteristics of composite thin film.

**Figure 3.** 3-dimensional AFM (20 x 20 μm$^2$) on glass substrate of (a) TiO$_2$-PTFE and (b) TiO$_2$-PDMS.
Table 2. Roughness Analysis of TiO$_2$-PTFE and TiO$_2$-PDMS surface

| Composite           | RMS (nm) |
|---------------------|----------|
| TiO$_2$-PTFE        | 12.50    |
| TiO$_2$-PDMS        | 11.74    |

Contact angle measurements are carried out using a liquid dropped on a glass surface coated with TiO$_2$-PDMS or TiO$_2$-PTFE. The liquid used is Rhodamin B. Photos of the droplets formed were analyzed using imageJ software to measure the contact angle. Based on these measurements obtained contact angles with various variations of the ratio of TiO$_2$: PDMS and TiO$_2$: PTFE before and after irradiation which can be seen in Table 3 below.

Table 3. Glass Contact Angles Before and After Irradiation

| No | Composite Variation | Contact angle (before) (°) | Contact angle (after) (°) |
|----|---------------------|-----------------------------|---------------------------|
| 1  | Glass without coating | 50.45                       | 48.8                      |
| 2  | Glass/TiO$_2$       | 69.62                       | 40.5                      |
| 3  | Glass/TiO$_2$-PDMS(1) | 128.85                     | 37.07                     |
| 4  | Glass/TiO$_2$-PDMS(2) | 126.15                     | 22.63                     |
| 5  | Glass/TiO$_2$-PDMS(3) | 123.5                      | 33.77                     |
| 6  | Glass/TiO$_2$-PDMS(4) | 133.47                     | 27.13                     |
| 7  | Glass/TiO$_2$-PDMS(5) | 133.15                     | 33.73                     |
| 8  | Glass/TiO$_2$-PTFE(1) | 115.23                     | 32.87                     |
| 9  | Glass/TiO$_2$-PTFE(2) | 116.32                     | 32.73                     |
| 10 | Glass/TiO$_2$-PTFE(3) | 117.27                     | 35.5                      |
| 11 | Glass/TiO$_2$-PTFE(4) | 117.37                     | 34.7                      |
| 12 | Glass/TiO$_2$-PTFE(5) | 108.77                     | 34.2                      |

The glass which was originally hydrophobic turned into hydrophilic after being exposed to ultraviolet light. The change in properties is caused by the occurrence of photocatalytic processes by thin layers of TiO$_2$-PDMS and TiO$_2$-PTFE. The hydrophilic nature can be achieved when stable hydroxyl forms gather on the surface. So that when there is water, the water is directly bound to the hydroxyl group. From this picture, it can be seen that the glass which is not coated and the glass which is only coated by TiO$_2$ experiences very small contact angle changes so that the glass does not yet have self-cleaning properties. While the glass coated by TiO$_2$-PDMS or the glass coated by TiO$_2$-PTFE has a significant angle change. TiO$_2$-PDMS(4) obtained the largest contact angle of 133.47°. The contact angle changes to 27.13° after exposure to light. While the TiO$_2$-PTFE(4) obtained the largest contact angle of 117.37°. The contact angle changes to 34.7° after exposure to light. This indicates that the glass coated by TiO$_2$-PTFE has high self-cleaning properties. This result is in line with research conducted by Tavares et al [5] and Kamegawa et al [6] where glass coated with TiO$_2$-PDMS has a contact angle of more than 80°, whereas glass coated by TiO$_2$-PTFE has a contact angle of 111°.

The glass coated with TiO$_2$-PDMS and the glass coated with TiO$_2$-PTFE were tested for self-cleaning ability by dripping 5 mL of rhodamin B 10 ppm on the glass and then irradiated using a 300 watt halogen lamp with a certain irradiation time. The self-cleaning activity test of glass coated with
TiO$_2$-PDMS and TiO$_2$-PTFE with varying irradiation time with various compositions of TiO$_2$: PDMS and TiO$_2$: PTFE can be seen in Figure 4a and 4b.

![Figure 4. Rhodamin B Degradation Results on coated Glass (A = TiO$_2$-PDMS, B = TiO$_2$-PTFE).](image)

The figure shows from this graph that it can be seen that glass coated by TiO$_2$-PDMS and TiO$_2$-PTFE has a higher decrease in absorbance than glass coated only by TiO$_2$. TiO$_2$-PDMS(3) has the greatest ability to degrade rhodamine B that is 37.04%, while the TiO$_2$-PTFE(4) has the greatest ability to degrade rhodamine B that is 47.67%. The increase in composite self-cleaning activities can be seen from the declining trend. Decreased absorbance of rhodamine B with increasing exposure time from 5 minutes to 20 minutes. This shows that the long exposure time will increase the self-cleaning activity on the composite. These results are in line with research conducted by Sunardi et al [11]. where the longer the glass is exposed to light, the smaller the absorbance value.

4. Conclusion

Coatings of TiO$_2$-PDMS and TiO$_2$-PTFE composites on glass substrates affect the hydrophobicity and hydrophilicity of the glass surface. Coating can increase the hydrophobicity of the glass surface. The glass coated by TiO$_2$-PDMS and TiO$_2$-PTFE has hydrophobic properties and after exposure to light it turns into hydrophilic. TiO$_2$-PDMS(4) the contact angle was 133.47°. The contact angle changes to 27.13° after exposure to light. In the TiO$_2$-PTFE(4) the contact angle was 117.37°. The contact angle changes to 34.70° after exposure to light. Addition of PDMS and PTFE to TiO$_2$ particles can increase the self-cleaning activity of TiO$_2$ on glass. The TiO$_2$-PDMS(3) was able to degrade rhodamine B by 37.04%, while the TiO$_2$-PTFE(4) was able to degrade rhodamine B by 47.67%.

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