Self-Cleaning Limestone Paint Modified by Nanoparticles TiO$_2$ Synthesized from TiCl$_3$ as Precursors and PEG6000 as Dispersant

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Abstract

Limestone is commonly used for wall painting, but it is easy to be dirty. In this study, a self-cleaning limestone paint was synthesized by modifying dispersant and TiO$_2$ nanoparticles. The TiO$_2$ that prepared by TiCl$_3$ were functionalized with PEG6000 as a surface activating agent. The paint achieved highest impurity degradation of 83.11% for the mass ratio of TiO$_2$ and PEG6000 (MRTP) of 1:6, in which TiO$_2$ average size distribution was 75.81 µm$^2$, the particle surface area of TiO$_2$ was 2,544 µm$^2$, and the smallest contact angle was 7°. It was found that the dispersant (PEG6000) significantly improved the self-cleaning ability of limestone paint. The surface tension reduction from PEG6000-modified prevented the agglomeration process of TiO$_2$ and suggests that the limestone paint a good self-cleaning coating for wall painting. Copyright © 2017 BCREC Group. All rights reserved

Keywords: TiO$_2$ photocatalyst; PEG6000 dispersant; limestone; self-cleaning


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1. Introduction

Limestone (CaCO$_3$ crude) is a minimal stone that predominantly found in the tropical regions with Madura Island-Indonesia as one of the most famous producers. The properties of limestone as coating agent makes the people there use it as a wall painting [1]. Besides easy to fabricate, it is also inexpensive and hard to peel off [2]. However, limestone is a pigment adsorptive so the paint relatively easy to be dirt.

That is why currently there are some researchers modify limestone paint to be self-cleaning. There have been some researches used to modify the properties of limestone paint. One of the most chosen methods is photocatalysis with TiO$_2$ as the material. Photocatalysis is a process where the sunlight breaks the molecules of organic impurities [3]. It is followed by the super-hydrophilic surface (contact angle ~0) [4] which leads to the reduction of surface tension that can easily be carried by water contact [5] [6]. TiO$_2$ it self is commonly taken from the commercial material, which makes the paint is not economically feasible. In this study, TiCl$_3$ was used as a precursor to synthesize TiO$_2$ [7].
However, the TiO$_2$ particles tend to microscopically agglomerate than making a thin film [8]. Therefore, a dispersant is needed to coat the particles so the film distribution going well [9]. In this study, the appropriate precision amount of PEG6000 was chosen as dispersant material [10]. Over dispersant composition will cover the film top thick. So, the particle can not be functionalized properly [11].

Therefore, this research observed the influence of the TiO$_2$ nano particle made from the TiCl$_3$ precursor and investigated the optimum composition of TiO$_2$:PEG6000 to prepare the self-cleaning limestone based paint.

2. Materials and Methods

The material used in this experiment were TiCl$_3$ (Merck, 15%), HCl 37%, NH$_4$OH (Merck, 28%), PEG6000 (Merck), limestone paint, and asbestos board. The TiO$_2$ nanoparticles were synthesized from precursor TiCl$_3$ by precipitation method [12]. To obtain anatase phase, calcination of TiO$_2$ was used at 400 $^\circ$C for 4 hours and was recalcined at 500 $^\circ$C for 2 hours due to the size that obtained was too small or it was still in the amorphous phase. Moreover, to obtain rutile phase, calcination of TiO$_2$ was used at 1000 $^\circ$C for 7 hours [12]. After the anatase and rutile phase was obtained, the XRD analysis of TiO$_2$ was conducted.

The suspension of TiO$_2$ was obtained by mixing TiO$_2$ and 10 mL aquadest. Then they were mixed by using magnetic stirrer at 50 $^\circ$C for 2 hours. The mass composition ratio of TiO$_2$ anatase: rutile was 9:1 gram. Then a predetermined amount of PEG6000 was added. In this experiment, it was determined that the mass ratio of TiO$_2$ and PEG (MRTP) were 1:2, 1:3, 1:4, 1:5 and 1:6 gram. Then, the substance was stirred by using magnetic stirrer for 30 minutes. Next, it was the FTIR analysis, which determines the type of chemical bond TiO$_2$/PEG6000. The 50 mg of TiO$_2$/PEG suspension was obtained by mixing using a magnetic stirrer for about 30 minutes.

The result was tested by using two methods, contact angle test, and self-cleaning test. Contact angle test was done by using three different conditions which are under the direct sunlight, under the UV light, and inside the room. The self-cleaning test was done by using mud as the impurity object at three different conditions which are under the direct sunlight, under UV light, and inside a room. The impurities added samples were then dried for 40 hours and were taken by photos every 10 hours interval.

3. Results and Discussion

3.1 XRD characterization

The XRD patterns (Fig. 1a) are for the calcined TiO$_2$ at 400 $^\circ$C for 4 hours. From that heating process, the amorphous TiO$_2$ powder was obtained and had no arising peak in which its particle size could not be determined. Therefore, the sample was reheated at 500 $^\circ$C for 2 hours was succeed become anatase phase (Fig. 1a). The spectrum in Fig. 1a has some coincide with JCPDS standard 00-021-1272 and 00-004-9552 data at 2$\theta$ = 25.52', 48.23', and 73.11'. From that sample, it could be seen that the TiO$_2$ was an anatase phase and the size was 7-15 nm. In Fig. 1b, the XRD patterns that were calcined TiO$_2$ at 1000 $^\circ$C for 7 hours. The spectrum of Fig. 1b had some coincide with JCPDS standards 00-21-1276 on 2927.41', 36.07', 39.24', 41.28', 44.12', 54.38', 56.61', 62.76', 64.12', 69.83', and 72.52'. So, the calcining process successfully made rutile phase with 80-99 nm particle size [12].

3.2 FTIR characterization

Infrared spectra of TiO$_2$/PEG 6000 suspen-
sion (Fig. 2) shows peaks in the wavelength of 940 cm\(^{-1}\), 1080 cm\(^{-1}\), 1200 cm\(^{-1}\), 1630 cm\(^{-1}\), and 3300 cm\(^{-1}\). This result shows that the making TiO\(_2\)/PEG6000 suspension was successful and there were bonds between TiO\(_2\) and PEG [8]. The presence of blending bonds between TiO\(_2\) and PEG was confirmed by FTIR spectrum from reference as shown in Table 1 [13].

### 3.3 Contact angle test

Fig. 3 shows that the TiO\(_2\) added paint had smaller water contact angle than the pure paint. The more addition of PEG the smaller of value contact angle on the paint surface. Meanwhile, the TiO\(_2\) layer without the addition of PEG had the highest value of contact angle. This condition happens due to the absence of hydroxyl on the substance, which eventually made water couldn’t go through the interior area in the film layer [4]. The condition of the measurement also was affected by the result of the contact angle in which three conditions were conducted to get a different distribution of the sunlight. The smallest contact angle value for direct sunlight was 7° in the sample with the MRTP is 1:6 gram. This condition was occurred due to the exposure of sunlight to the TiO\(_2\). It would photocatalytic process in which the reaction made the contact angle of the water decrease and become hydrophilic [14].

### 3.4 Self-cleaning test

Self-cleaning test was conducted in 5 days by spraying water to the sample each day every 10 hours as shown in Table 2. The pictures shown in Fig. 4 are the qualitative result of impurity reduction. The self-cleaning test result shown that the cleanest sample was the sixth sample (Fig. 4), with the MRTP was 1:6 under direct sunlight and the percentage of highest degradation impurity area was 83.11%. It was shown the process of degradation impurities in that composition was succeeded better and faster than the other samples. Meanwhile, the impurity in the sample 0 (without TiO\(_2\)) still remained and tend to be stable. In that case, the addition of TiO\(_2\) on the paint would give the self-cleaning ability to the paint. It proved that the pure limestone paint would not be sufficient to clean the impurity on the paint itself (self-cleaning ability).

Figure 5 showed the impurity that had been degraded on every condition of the samples. It was seen that the graphic pattern under direct sunlight condition had the same pattern with under UV light condition and inside a room condition. The highest value of degradation impurity area was in the sample with the MRTP was 1:6 with 0.0257 (cm\(^2\)/minutes) impurities degradation. The lowest degradation impurity

### Table 1. Wavenumber and functional group of anatase and rutile phase and PEG6000

<table>
<thead>
<tr>
<th>Phase</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>1,210.92</td>
<td>Ti–O–O Vibration</td>
</tr>
<tr>
<td></td>
<td>1,636.61</td>
<td>Bending vibration of H(_2)O and Ti–OH</td>
</tr>
<tr>
<td></td>
<td>2,360.83</td>
<td>Defect (CO(_2) vibration)</td>
</tr>
<tr>
<td></td>
<td>3,357.26</td>
<td>H–OH</td>
</tr>
<tr>
<td>Rutile</td>
<td>2358.65</td>
<td>Defect (CO(_2) vibration)</td>
</tr>
<tr>
<td>PEG 6000</td>
<td>2880</td>
<td>Aliphatic stretching of CH</td>
</tr>
<tr>
<td></td>
<td>1470</td>
<td>Bending vibration of CH</td>
</tr>
<tr>
<td></td>
<td>1100</td>
<td>C–O Alcohol</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>Vibration of C–C</td>
</tr>
</tbody>
</table>

**Figure 2.** Infrared spectra of TiO\(_2\)/PEG6000

**Figure 3.** Contact angle result on paint surface
area was in the sample 0 (pure limestone paint without TiO$_2$). The more dispersant added the better self-cleaning ability of the paint.

Based on the result, drying process condition would affect the self-cleaning ability that has been produced, in which received three different conditions of UV light distribution. The percentage value of impurity degradation under direct sunlight would have the highest impurity percentage. This condition happened due to the extensive exposure to the UV light.

**Table 2.** The self-cleaning result test for each condition

<table>
<thead>
<tr>
<th>Condition</th>
<th>TiO$_2$:PEG Mass (gram)</th>
<th>Percentage of impurity degraded (%)</th>
<th>Rate of degradation impurities (cm$^2$/minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunlight</td>
<td>0</td>
<td>29.19</td>
<td>0.0085</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>55.71</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>83.43</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>73.03</td>
<td>0.0199</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>78.66</td>
<td>0.0249</td>
</tr>
<tr>
<td></td>
<td>1:6</td>
<td>83.11</td>
<td>0.0257</td>
</tr>
<tr>
<td>UV</td>
<td>0</td>
<td>16.63</td>
<td>0.00499</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>19.77</td>
<td>0.00547</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>48.19</td>
<td>0.0137</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>28.66</td>
<td>0.00885</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>32.23</td>
<td>0.00969</td>
</tr>
<tr>
<td></td>
<td>1:6</td>
<td>52.38</td>
<td>0.0155</td>
</tr>
<tr>
<td>Indoor</td>
<td>0</td>
<td>15.36</td>
<td>0.0045</td>
</tr>
<tr>
<td></td>
<td>1:2</td>
<td>17.93</td>
<td>0.00511</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
<td>22.67</td>
<td>0.00559</td>
</tr>
<tr>
<td></td>
<td>1:4</td>
<td>16.16</td>
<td>0.00491</td>
</tr>
<tr>
<td></td>
<td>1:5</td>
<td>18.41</td>
<td>0.00585</td>
</tr>
<tr>
<td></td>
<td>1:6</td>
<td>37.02</td>
<td>0.0119</td>
</tr>
</tbody>
</table>

**Table 3.** AFM Image Processing result

<table>
<thead>
<tr>
<th>TiO$_2$: PEG Mass</th>
<th>Area of TiO$_2$ (µm$^2$)</th>
<th>Average Size of TiO$_2$ (µm$^2$)</th>
<th>Percent Area of TiO$_2$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:3</td>
<td>1786</td>
<td>77.1</td>
<td>59.53</td>
</tr>
<tr>
<td>1:4</td>
<td>1321</td>
<td>67.09</td>
<td>44.03</td>
</tr>
<tr>
<td>1:6</td>
<td>2544</td>
<td>75.81</td>
<td>63.6</td>
</tr>
</tbody>
</table>

**Figure 5.** The influence of TiO$_2$:PEG mass comparison to the percentage impurity area in every condition.
to the TiO$_2$ the better the photocatalytic process [15].

3.4 AFM test

The TiO$_2$ dispersion test was conducted in the sample with the MRTP is 1:3, 1:4, and 1:6. ImageJ software was used to determine TiO$_2$ dispersion by measuring particle area of TiO$_2$, percent and the average size of the TiO$_2$ particle. The result of TiO$_2$ dispersion test using Atomic Force Microscope (AFM) shows in Fig. 6, the morphology surface reveals the nanocrystalline TiO$_2$ [16]. Table 3 shows that from all the three samples with different dispersant variation mass of PEG that sample MRTP was 1:6 had the highest TiO$_2$ distribution with average size 75.81 (µm$^2$) and particle area of TiO$_2$ 2,544 (µm$^2$) and percent area 63.6%. Distribution of TiO$_2$ on the paint film surface would affect the photocatalytic process that happened, the more dispersion of TiO$_2$ spread evenly the photocatalytic process getting better.

![AFM analysis result with MRTP](image)

**Figure 6.** The AFM analysis result with MRTP is (a) 1:3, (b) 1:4, and (c) 1:6

![Condition of sprayed sample after drying process](image)

**Figure 4.** Condition of sprayed sample after drying process (i) under direct sunlight, (ii) under UV light, (iii) Inside a room (a) before drying process, (b) After one day drying process, (c) After 2 days drying process, (d) After 3 days drying process, (e) After 4 days drying process
4. Conclusions

A super-hydrophilic self-cleaning limestone paint was successfully prepared by adding TiO$_2$ nanoparticles made from the TiCl$_3$ precursor. After being modified with PEG6000 for perfect particle distribution purpose, the particle showed good hydrophilicity with water contact angles $\approx 7^\circ$. The composition TiO$_2$:PEG6000 of 1:6 exhibited highest impurity degradation of 83.11% with TiO$_2$ average size distribution was 75.81 µm$^2$ and particle area 2544 µm$^2$. It was found that dispersant (PEG6000) significantly improved the self-cleaning ability of limestone paint. The surface tension reduction from PEG6000-modified prevented the agglomeration process of TiO$_2$ and makes the limestone paint a good self-cleaning coating for wall painting.

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