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Research Article

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.

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 superhydrophilic 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].

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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_4OH (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 °C for 4 hours and was recalcined at 500 °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 °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 °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 °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 °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 2θ = 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 °C for 7 hours. The spectrum of Fig. 1b had some coincide with JCPDS standards 00-21-1276 on 2θ27.41°, 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-

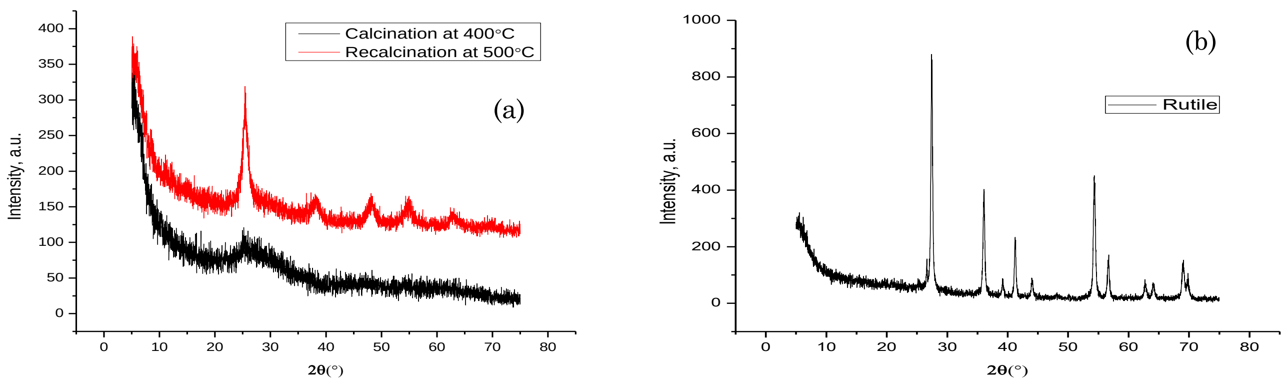


Figure 1. XRD pattern of nanoparticle TiO_2 : a) anatase, b) rutile

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].

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

Phase	Wavenumber (cm^{-1})	Functional Group
Anatase	1,210.92	Ti–O–O Vibration
	1,636.61	Bending vibration of H_2O and Ti–OH
	2,360.83	Defect (CO_2 vibration)
	3,357.26	H–OH
Rutile	2358.65	Defect (CO_2 vibration)
PEG 6000	2880	Aliphatic stretching of CH
	1470	Bending vibration of CH
	1100	C–O Alcohol
	950	Vibration of C–C

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

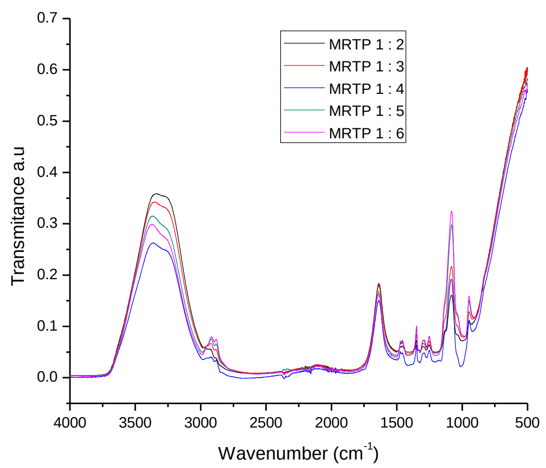


Figure 2. Infrared spectra of TiO_2/PEG6000

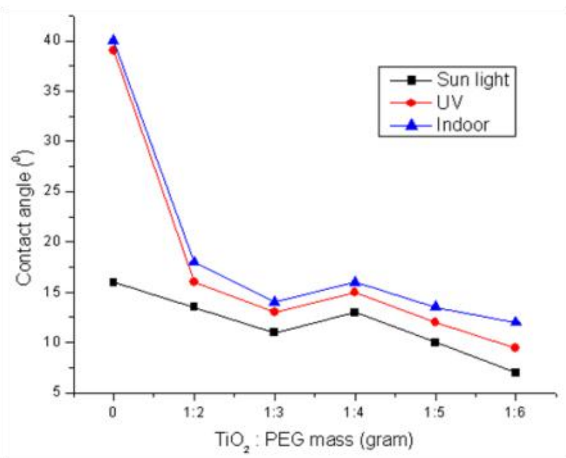


Figure 3. Contact angle result on paint surface

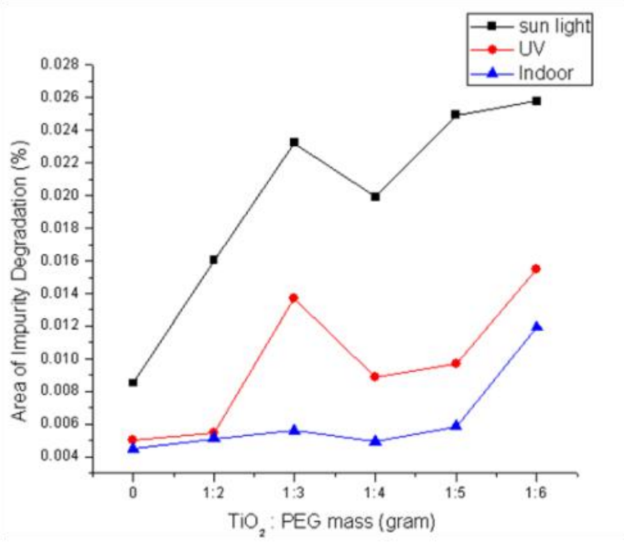


Figure 5. The influence of TiO_2:PEG mass comparison to the percentage impurity area in every condition

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 3. AFM Image Processing result

TiO_2: PEG Mass	Area of TiO_2 (μm²)	Average Size of TiO_2 (μm²)	Percent Area of TiO_2 (%)
1:3	1786	77.1	59.53
1:4	1321	67.09	44.03
1:6	2544	75.81	63.6

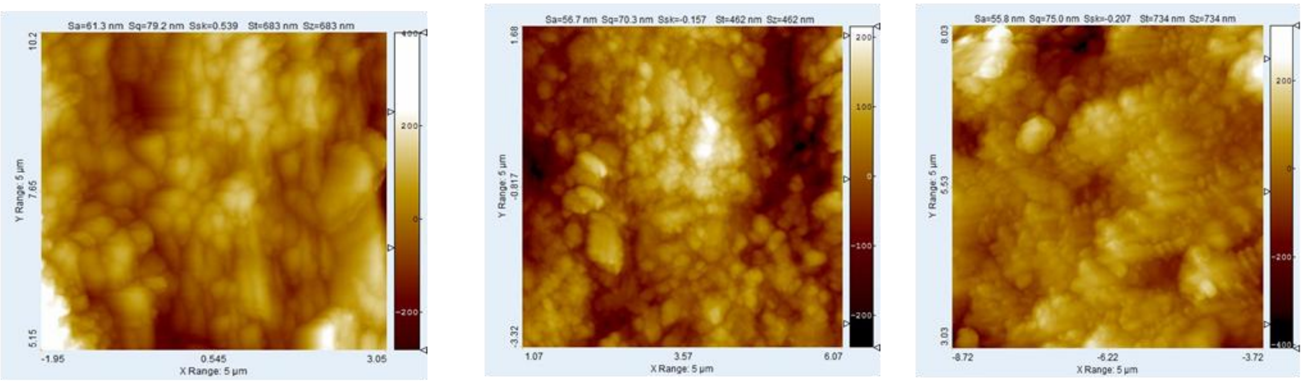
Table 2. The self-cleaning result test for each condition

Condition	TiO_2:PEG Mass (gram)	Percentage of impurity degraded (%)	Rate of degradation impurities (cm²/minutes)
Sunlight	0	29.19	0.0085
	1 : 2	55.71	0.016
	1 : 3	83.43	0.023
	1 : 4	73.03	0.0199
	1 : 5	78.66	0.0249
	1 : 6	83.11	0.0257
UV	0	16.63	0.00499
	1 : 2	19.77	0.00547
	1 : 3	48.19	0.0137
	1 : 4	28.66	0.00885
	1 : 5	32.23	0.00969
	1 : 6	52.38	0.0155
Indoor	0	15.36	0.0045
	1 : 2	17.93	0.00511
	1 : 3	22.67	0.00559
	1 : 4	16.16	0.00491
	1 : 5	18.41	0.00585
	1 : 6	37.02	0.0119

to the TiO_2 the better the photocatalytic process [15].

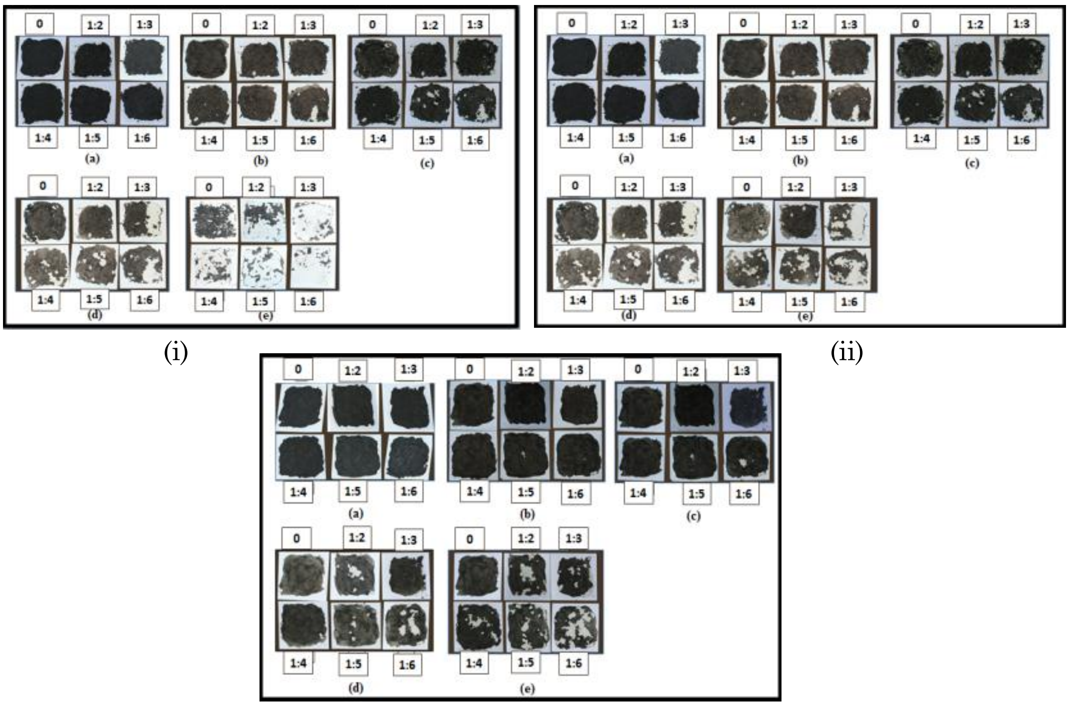
3.4 AFM test

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.



(a) (b) (c)

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



(i) (ii)

(iii)

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 ~7°. 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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