Synthesis and Characterization of Nano TiO$_2$ with Sol-Gel Method as Self-Cleaning Agent on Acrylic Paint

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Abstract—Metal oxide TiO$_2$ has photocatalytic properties that make TiO$_2$ amphilic, that is, hydrophobic in the dark (without UV light) and hydrophilic in the light (there is UV light). The photocatalytic properties of TiO$_2$ can be utilized to develop self-cleaning materials in paints. Self-cleaning material is a material capable of cleaning itself both by avoiding it and by degrading the dirt that clings to it with the help of UV rays. The TiO$_2$ nano particle synthesis process uses the sol-gel method with the precursor tetrabuthyl titanate (TBT). The purpose of this research is to synthesize TiO$_2$ nano particles as self-cleaning material in paint with the most appropriate composition. The results obtained from the synthesis of nano TiO$_2$ particles were tested by FTIR and appeared at a peak of 467.50 cm$^{-1}$ indicating the presence of TiO$_2$ groups. In addition, characterization using XRD was also produced which make TiO$_2$ amphilic, that is, hydrophobic properties through contact angle measurements and the best contact angle values obtained on TiO$_2$ / paint (2: 8) were 102.2$^\circ$.

Keywords—nano TiO$_2$, sol-gel, self-cleaning, hidrofobic

I. INTRODUCTION

Currently the development of nanoparticle technology has been widely used in various purposes, one of which is as a developer of self-cleaning properties. Self-cleaning properties are properties where a material is able to clean itself both by avoiding it and by degrading the dirt that adheres to itself. One of these self-cleaning properties can be applied to wall paints. Wall paint used by the community is often difficult to clean from dirt or ink so self-cleaning properties need to be developed in the paint to simplify the maintenance process.

Development of the properties of paint is needed to overcome the above problems. The paint is expected to degrade the dirt or stains on the wall itself. This property is called "self-cleaning". Self-cleaning properties on the surface of the fabric work with the photocatalytic principle that works when the surface gets ultraviolet (UV) radiation. The photocatalysis process makes TiO$_2$ hydrophilic, which is very like water when exposed to UV rays, the impact of nano-sized TiO$_2$ surface remains transparent and not foggy when exposed to water vapor, while in the dark (no UV rays) TiO$_2$ is hydrophobic or does not like water. In a world of light and dark cycles, TiO$_2$ behaves amphilic, hydrophobic when dark and hydrophilic when bright [1].

The mechanism of the amphilic properties of TiO$_2$ occurs due to the presence of UV light. The presence of UV light on TiO$_2$ results in the transition of electrons (e$^-$) from the valence band to the conduction band, thus producing a vacancy (h$^+$) on the valence band and electrons (e$^-$) on the conduction band. Electrons reduce Ti (IV) to Ti (III), while a vacuum (h$^+$) oxidizes O$_2$ to O$_2^-$ resulting in an oxygen vacuum on the surface. The oxygen vacuum is filled with water molecules that bind with Ti (III) which then decomposes into hydroxo on the surface. Furthermore, the hydroxo undergoes condensation by releasing water to form a hydrophilic Ti-O-Ti bond [2].

The development of TiO$_2$ nano particle synthesis method is needed to control the crystalline phase, size, and morphology of TiO$_2$ nanocrystals. Synthesis of TiO$_2$ nanoparticles can be done by the sol-gel method. The sol-gel method is a method of synthesis of nanoparticles where in the process a phase change occurs from a colloidal suspension (sol) forming a continuous liquid phase (gel). The advantages of the sol-gel method for the synthesis of metal oxide nanoparticles include forming a transparent oxide layer that adheres perfectly to the fabric, resulting in uniform particle size distribution and a large surface area [3].

This research study the self-cleaning activity of paint based on TiO$_2$. Mixing paint with TiO$_2$ will be carried out with different volume ratio of TiO$_2$/paint of 0.5: 9.5; 1: 9; 1.5: 8.5; and 2:8. The characterization of TiO$_2$ nanoparticles are tested using X-Ray Diffraction (XRD) and Fourier Transform Infra Red (FTIR) instruments. The self-cleaning test is measured by the strength of the hydrophobic activity.
obtained by measuring the angle of contact of water with the paint / TiO2 coated glass surface.

II. METHODS

A. Tool

The tools used in this study are glass, dropper pipette, beaker, measuring cup, hot plate stirrer, magnetic stirrer, spatula, watch glass, mortal and pestle, analytical balance. Furnace, oven (Binder, Germany), scanning electron microscopy (SEM-EDX, Philips XL30; Germany), Fourier Transform Infrared Spectrophotometer (Shimadzu 8021), universal pH indicator, X-Ray Diffraction (Shimadzu XRD 6000).

B. Material

The materials used in this research are TBT (Tetrabuthyl Titanate) (Sigma-Aldrich), white acrylic paint, ethanol pro-analyst, glacial acetic acid and aquades.

III. PROCEDURE

A. Synthesis of TiO2 nanosols

The manufacture of nano TiO2 particles was carried out by the sol-gel method using TBT as precursors, aquades, p.a ethanol and glacial acetic acid. Nano sol was obtained by mixing Tetrabuthyl Titanate (TBT) and ethanol p.a and then sterilizing it for 30 minutes at room temperature and a clear yellow solution was obtained. The solution was then added to a mixture of glacial acetic acid, distilled water and ethanol p.a dropwise (± 1 drop / second) with strong stirring. The mixture is then stirred for 1 hour and a clear yellow light sol is produced. The solution is then left in ambient conditions for 24 hours. After being simulated for 24 hours, the sol-gel Tis dried at 110ºC to convert the sol-gel phase to powder and is ground for 2 hours at 500ºC. The powder formed was characterized by FTIR and XRD [4].

B. Chemical Characterization of TiO2 nanosols with FTIR

Chemical characteristics of TiO2 nanosols was analyzed using FTIR spectrophotometer. The FTIR spectrum of functional group of TiO2 was shown in Figure 1.

Fig. 1. FTIR spectra of TiO2 synthesized by TiO2

Based on the results obtained from the FTIR test in Figure 1 shows the peaks that appear on several waves. The FTIR spectrum on TiO2 shows the peak at wave number 3418.39 cm⁻¹ which is the absorption of the stretching –OH vibration, while the absorption of 1638.21 cm⁻¹ which is the absorption of the bend –OH vibration. Based on the research that has been carried out the bend -OH vibration of the Ti-OH bond at the peak of 1650 cm⁻¹ resulted from H2O molecular adsorbent that is not completely released after synthesis by the sol-gel method, whereas, at the peak of 3250 cm⁻¹ is stretching vibration absorption -OH group of Ti-OH. The next spectrum appears at the peak of 467.50 cm⁻¹ indicating the presence of Ti-O bonds.

TABLE I. FUNCTIONAL GROUP DATA ON TiO2 NANOSOLS

| Functional group | Wave Number |
|------------------|-------------|
| Vibratory Ti-O from TiO2 | 467,50 |
| OH buckling vibrations from Ti-OH | 1638,21 |
| Stretching –OH vibrations from Ti-OH and ethanol | 3418,39 |

E. Self-Cleaning Test with Contact Angle measurement

Paint with the addition of TiO2 coated glass was then measured by contact angle by means of a test of water drops on the glass surface. The drip results were then photographed using a Canon Ixus 230HS camera. Images from this shoot are then analyzed using the AutoCAD application to measure the angle of contact between water and glass surface.

IV. RESULTS AND DISCUSSION

A. Synthesis of TiO2 nanosols

In the TiO2 nanosol synthesis process hydrolysis and condensation reactions occur. In the hydrolysis stage, the reaction takes place quickly where there is a change of alkoxide groups with nucleophilic hydroxyl groups. At the condensation stage it will produce the formation and growth of TiO2.xH2O [5].

B. Characterization of TiO2 nanosols with FTIR

Chemical characteristics of TiO2 nanosols was analyzed using FTIR spectrophotometer. The FTIR spectrum of functional group of TiO2 was shown in Figure 1.
C. Characterization of TiO₂ nanosols by X-ray diffraction (XRD)

The results of the peak angle XRD test that appeared were matched with JCPDS and the anatase phase was obtained. This was evidenced by the presence of typical anatase peaks seen at an angle of 2θ = 25.0707° with an intensity of 100% and at several other peaks corresponding to JCPDS anatase with number 21-1272. Scherrer equation (1) was used to calculate particle size of the TiO₂.

\[ D = \frac{0.94 \lambda}{\beta \cos \theta} \]  

where:
- \( D \) = crystal size
- \( \lambda \) = wavelength of X-ray beam
- \( \beta \) = FWHM (full width half maximum) / intensity in radians
- \( \theta \) = large angle from peak with high intensity.

The particle size of TiO₂ obtained from synthesis was 24.32 nm.

![Fig. 2. Synthesis of XRD TiO₂ data (XRD Philips X-Pert Powder Diffractometer)](image)

D. Self-Cleaning Test Results with Contact Angle measurements

The ability of self-cleaning paint with the addition of TiO₂ can be measured by how high the hydrophobic value of the paint produced when coating a media. Contact angle measurement of Paint / TiO₂ coated on glass media was reported in the Table 2.

| Sample         | Drop Test Results | Contact Angle |
|----------------|-------------------|---------------|
| Paint          |                   | 62.6°         |
| Paint + TiO₂   | 0.25 gr           | 67.6°         |
| Paint + TiO₂   | 0.50 gr           | 61.0°         |
| Paint + TiO₂   | 1.00 gr           | 86.1°         |
| Paint + TiO₂   | 1.50 gr           | 72.3°         |
| Paint + TiO₂   | 2.00 gr           | 102.2°        |

![Fig. 3. Surface morphology of TiO₂ Paint](image)

The results of the test drops on paint without TiO₂ showed that the glass has a small contact angle because when the water drops the paint is not round and the angle is 62.6°. The 62.6° angle shows that this glass is not hydrophobic because there are still many interactions of water with the glass surface. The condition for an object to be called hydrophobic is if it forms an angle of >90°, whereas for an object having a contact angle <90° then the object is hydrophilic [6].

The results of the test drops on the glass coated with paint/TiO₂ with several variations of the mixture showed that the glass coated with paint/TiO₂ with several variations of the mixture produced contact angles with a greater value compared to the contact angle values produced by the paint alone although the results were not significant. Paint / TiO₂ coated glass (9.25: 0.25), (9.5: 0.5), (9: 1), (8.5: 1.5), and (8: 2), produce a value The contact angles were 67.6°, 61.0°, 86.1°, 72.2° and 102.2° respectively. The contact angle value in the paint / TiO₂ composition has exceeded 90° so that the resulting paint is already hydrophobic.

The hydrophobic nature of the paint increases with increasing mass of TiO₂ added. This happens because the more TiO₂ is added to the paint, the more nano TiO₂ coats the surface so that nano-sized TiO₂ will hold water from dripping so it won't wet the surface. This is based on the lotus effect on taro leaves. Taro leaves have a nano-sized layer, this layer makes taro leaves and lotus leaves not wet. The same principle is applied to surfaces coated with TiO₂ with nano size [7].

E. Morphological analysis of paint using Scanning Electron Microscopy (SEM)

Analysis using SEM was conducted to determine the surface morphology that formed on the surface of the paint.
The surface of the paint with the addition of TiO$_2$ was still a lump which indicates that the mixing of the paint and TiO$_2$ was still not evenly distributed perfectly, causing a difference in the contact angle values when the paint is tested for hydrophobic properties between one surface and another.

SEM-EDX analysis of paint with the addition of TiO$_2$.

Fig. 4. Analysis of EDX paint with the addition of TiO$_2$

Figure 4 shows that TiO$_2$ was found in paint. In paint with the addition of TiO$_2$ shows that there was TiO$_2$ in the paint which indicated that the process of adding TiO$_2$ to the paint was successfully done because TiO$_2$ was embedded in the paint even though the results were less than maximal at only 3.4%.

V. CONCLUSIONS AND SUGGESTIONS

Conclusion

Based on the results of research and discussion it can be concluded that TiO$_2$ exhibit good self-cleaning activity in the paint. The hydrophobic properties of TiO$_2$ which is studied from water contact angle shows that the more TiO$_2$ added to the paint, the better the hydrophobic properties.

Suggestion

It is recommended to vary the mixing of paint with more TiO$_2$ so that the best results can be known.

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