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Synthesis and Characterization of Nano TiO_2 with Sol-Gel Method as Self-Cleaning Agent on Acrylic Paint

Maharani,D.K
Chemistry Department
Universitas Negeri Surabaya
Surabaya, Indonesia
dinakartika@unesa.ac.id

Setiarso, P
Chemistry Department
Universitas Negeri Surabaya
Surabaya, Indonesia
pirimsetiarso@unesa.ac.id

Anggarani, M.A
Chemistry Department
Universitas Negeri Surabaya
Surabaya, Indonesia
mirwa_adi@yahoo.com

A'yun, Q
Chemistry Department
Universitas Negeri Surabaya
Surabaya, Indonesia
qurrotul343@gmail.com

***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 produced the anatase crystalline phase of TiO_2 with a crystal size of 24.32 nm. Surface morphology was analyzed by Scanning Electron Microscopy (SEM). The ability of self-cleaning properties in paint was measured through hydrophobic properties through contact angle measurements and the best contact angle values obtained on TiO_2 / paint (2: 8) were 102.2^o.**

***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 hydroxso undergoes condensation by releasing water to form a hydrophobic 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 / TiO_2 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, Germani), 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 TiO_2 nanosols*

The manufacture of nano TiO_2 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 TiO_2 nanosols with FTIR*

The dried TiO_2 powder was taken several mg to be mixed with a few mg of dry KBr to be made pellet then analyzed using FTIR.

C. *Characterization of TiO_2 nanosols by X-ray diffraction (XRD)*

The dried TiO_2 powder is taken several mg for testing and analyzed using X-ray diffraction (XRD) at an angle of 2θ 10º-100º.

D. *Mixing TiO_2 with Acrylic Paint and Coating on Glass Media*

TiO_2 powder that has been planted was then mixed with acrylic paint with a composition (gram) TiO_2 / Cat 0.5: 9.5; 1: 9; 1.5: 8.5; and 2: 8. Each mixing result was added with 2 mL of distilled water. The paint was then stirred with a spatula until evenly distributed and coated on glass that has been washed with distilled water and ethanol. Coating of paint / TiO2 on the glass is done by the smear method.

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 TiO_2 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 $TiO_2.xH_2O$ [5].

B. *Characterization of TiO_2 nanosols with FTIR*

Chemical characteristics of TiO_2 nanosols was analyzed using FTIR spectrophotometer. The FTIR spectrum of functional group of TiO2 was shown in Figure 1.

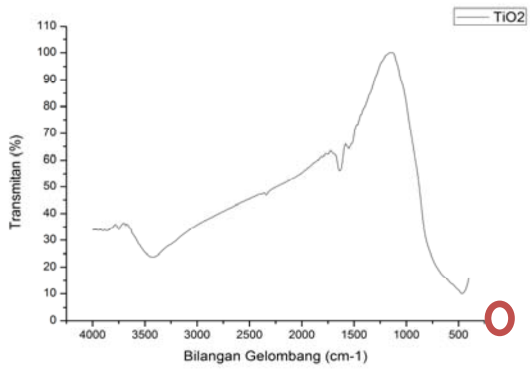

Fig. 1. FTIR spectra of TiO_2 synthesized by TiO_2

Based on the results obtained from the FTIR test in Figure 1 shows the peaks that appear on several waves. The FTIR spectrum on TiO_2 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 H_2O 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 TiO_2 nanosls

Functional group	Wave Number
Vibratory Ti-O from TiO_2	467,50
OH buckling vibrations from Ti-OH	1638,21
Stretching –OH vibrations from Ti-OH and ethanol	3418,39

C. *Characterization of TiO_2 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 = 25.0707º 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 TiO_2.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{.........(1)}$$

D = crystal size
λ = wavelength of X-ray beam
β = FWHM (full width half maximum) / intensity in radians
θ = large angle from peak with high intensity.
The particle size of TiO_2 obtained from synthesis was 24.32 nm.

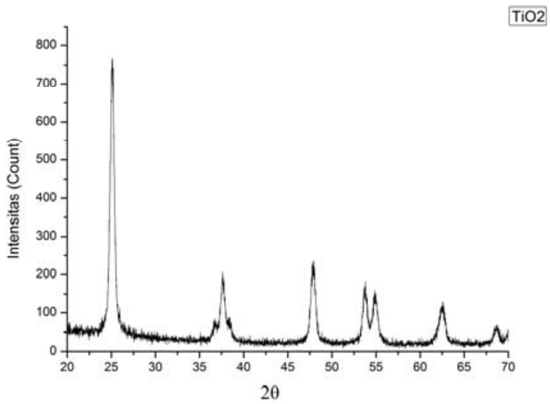

Fig. 2. Synthesis of XRD TiO2 data (XRD Philips X-Pert Powder Diffractometer)

D. *Self-Cleaning Test Results with Contact Angle measurements*

The ability of self-cleaning paint with the addition of TiO_2 can be measured by how high the hydrophobic value of the paint produced when coating a media. Contact angle measurement of Paint / TiO_2 coated on glass media was reported in the Table 2.

TABLE II. DATA OF CONTACT ANGLE TEST RESULT

Sample	Drop Test Results	Contact Angle
Paint		62,6º
Paint + TiO_2 0,25 gr		67,6º
Paint + TiO_2 0,50 gr		61,0º
Paint+ TiO_2 1,00 gr		86,1º
Paint + TiO_2 1,50 gr		72,3º
Paint + TiO_2 2,00 gr		102,2º

The results of the test drops on paint without TiO_2 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/TiO_2 with several variations of the mixture showed that the glass coated with paint/TiO_2 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 / TiO_2 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 / TiO_2 composition has exceeded 90° so that the resulting paint is already hydrophobic.

The hydrophobic nature of the paint increases with increasing mass of TiO_2 added. This happens because the more TiO_2 is added to the paint, the more nano TiO_2 coats the surface so that nano-sized TiO_2 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 TiO_2 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.

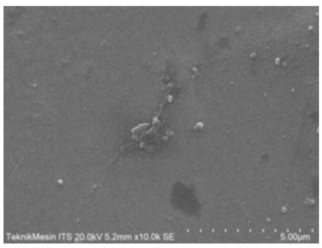

Fig. 3. Surface morphology of TiO_2 Paint

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.

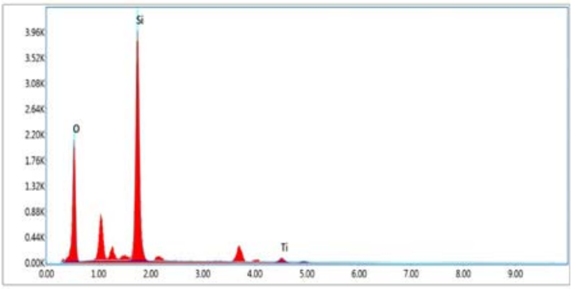

Fig. 4. Analysis of EDX paint with the addition of TiO_2

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 angel 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 TiO2 so that the best results can be known.

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