

The Study of Self-Cleaning Properties of TiO₂ Coated on Cotton Fabrics

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Abstract— This research study about self cleaning activity of TiO₂ coated on cotton fabric. TiO₂ nanoparticles is known as good semiconductor which have photocatalytic properties. Cotton fabric was coated by TiO₂ to produce self cleaning textiles. Coating of TiO₂ nanoparticles on cotton fabrics was carried using a pad-dry-cure method with citric acid binder variation composition of 25%, 30%, 35%. And 40%. Characterization of TiO₂ coated fabrics was studied using EDX analysis and stiffness test, while self cleaning activity of coated fabrics was studied using color aging test. The results showed that the stiffness value of coated cotton fabrics were wasn't change significantly. The EDX analysis of the cotton fabric coated with TiO₂ nanoparticles showed more Ti were bonded to the fabric which is coated with 25% binder. Self cleaning activity showed that cotton fabric coated TiO₂ with composition 25% had the largest self cleaning activity.

Keywords— cotton fabrics, self cleaning activity, TiO₂

I. INTRODUCTION

The rapidly increasing human population is an opportunity for textile entrepreneurs to be able to produce textiles that have additional capabilities regardless of their primary use or commonly called multifunctional textiles. The multifunctional capabilities include textiles that are waterproof, anti-bacterial, anti-UV, self-cleaning, fire-proof and even bulletproof. These multifunctional capabilities can be produced by producers through the process of adding good new materials in ready-made textiles or initial textiles which are still in the form of fibers [1].

One of the multifunctional textiles that are in great demand by researchers is the nature of self-cleaning. The textile which has self-cleaning properties at the end of 2017 has been developed by researchers because human activities in the globalization era tend to be busy and prefer practical things. Self-cleaning activities will shorten the washing time because the dirt has been degraded by the help of the sun before washing is done. In addition, many other reasons are developed because Indonesia's climate and geographical location tend to have sufficient solar intensity to activate the degradation properties of self-cleaning.

This self-cleaning ability can be realized by modifying textiles with metal oxide compounds [2]. One of modifying process on textile is by coating method using photocatalytic nanoparticles such as TiO₂. The type of textile usually used in self cleaning study is cotton. Cotton cloth is popularly used because it has good characteristics for clothing materials that can be regenerated, biodegradable, soft, comfortable, warm, and hygroscopic [3].

The TiO₂ particles coating method on cotton fabrics widely used by previous studies basically has the disadvantage of using TiO₂ powder which is less efficient due to decreased TiO₂ activity [4]. The decrease in activity and concentration is influenced by the large size of TiO₂ particles in powder form. To overcome this problem, most photocatalyst semiconductor researchers make thin layers of semiconductors using methods such as the sol gel technique [5]. The coating of TiO₂ nano particles on cotton fabrics still has a problem that is the lack of strong or stable TiO₂ bonds to the fabric, so it is necessary to add a crosslinker or binder. Cotton fabrics consist of cellulose which has a high-OH functional group. This OH group will connected to TiO₂ through a binder. One of binder which can bond the OH and TiO₂ is citric acid. The alcohol group leads to the formation of covalent bonds as a result of the esterification reaction of the carboxylic group in citric acid [6]. The esterification reaction occurs when the hydroxyl group from alcohol will react with carboxylic acid compounds to produce esters. Karimi [7] have successfully done nano TiO₂ coating on a cotton fabric with succinic acid binder which has two carboxylic group .In this study the coating of TiO₂ on cotton fabrics used citric acid as a binder which has three carboxylic groups in order to make more bridge of cellulose functional group with TiO₂ nanoparticles.

Based on the description above, it is necessary to make TiO₂ nano particles with citric acid as a binder to be superimposed on a cotton fabric fiber. Citric acid coating will be done with several concentrations of 25 %, 30 %, 35 %, and 40 %. In this research the coated cotton fabrics characterization will be tested using EDX analysis and

stiffness test, meanwhile self-cleaning activity of coated cotton fabrics were obtained by color aging test.

II. RESEARCH METHODS

A. Tools

The tools used are in the form of beaker, measuring cup, measuring flask, dropper pipette, magnetic stirrer, porcelain cup, plastic bottle, mortar and pestle, 60 mesh sieve, destruction equipment, desiccator, tools used in this study is a pipette, beaker, measuring cup, hot plate stirrer, magnetic stirrer, spatula, watch glass, analytical balance, glassware, scissors, ultrasonic (220V, 800 W, 40 kHz, Turkey). Oven (Binder, Germani). UV-A lamps (15 W, Philips, Belgium), scanning electron microscopy (SEM-EDX, Philips XL30; Germany)

B. Material

The materials used in this study were white 100% cotton fabrics, citric acid and sodium hypopospit from Merck ChemicalCo., Germany. Titananiumisopropoxide (TTIP) 97% (Sigma-Aldrich), 0.1 M HCl, aquades, Ethanol 96 % (Merck), food coloring stains Ponceau 4R.

III. RESEARCH PROCEDURE

A. Preparation of TiO₂ Nano Particles

Preparation of nano TiO₂ particles was carried out by the sol-gel method using TTIP as precursor, ethanol p.a and 0.1 M HCl. The volume composition was 97 mL ethanol p.a, HCl. Ethanol and HCl are put into a beaker, then added drop by drop and carried out in ultrasonic. Next in ultrasonic during 4 hours later left in ambient conditions for 24 hours.

B. Coatings of Citric Acid on cotton Fabrics

Prepare a solution with different concentrations of citric acid that is 25 g / L, 30 g / L, 35 g / L, and 40 g / L. Citric acid was put into a beaker, then added with NaH₂PO₂ as a catalyst as much as 18 g / L. The cotton fabric were then soaked in the mixture and performed ultrasonic for 30 minutes at a temperature of 30-40 °C. The cotton cloth is aerated for 15 minutes [8].

C. Coating of TiO₂ on Cotton Fabrics

Previously TiO₂ nano particle solution was cultivated for 30 minutes. Cotton fabrics that has been coated with citric acid was dipped into TiO₂ nanosol for 25 seconds [9]. After that the fabrics was dried at 80 ° C for 5 minutes then cured at 140 °C for 3 minutes until the TiO₂ nano particles were completely bound to the fabric [10]. The coated fabric is then analyzed using EDX and stiffness test.

D. Self Cleaning Activity Testing

Self-cleaning test on cotton fabrics was done by dripping food coloring stains Ponceau 4R 10 mg / L with a distance of 1 cm above the cloth and dried at room temperature. To test the ability of UV light to degrade stains, the sample was irradiated with a 15 Watt UV lamp, which can be done using a laminar lamp for 5 hours. The total color difference before and after irradiation was carried out using a reflectance spectrophotometer. Measurements were made

using the CIE Lab 1970 color space system. Test samples were measured for reflectance (% R) at a wavelength of 400 - 700 nm with an interval of 20 nm so that a maximum wavelength can be determined with a value The lowest% R, and the reflectance value is converted to the color aging value (K / S) based on the Kubelka-Munk equation as follows:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R}$$

Information:

K: Light absorption coefficient

S: Scattering coefficientlight

R: % reflectance

IV. RESULTS AND DISCUSSION

In this section, the results of TiO₂ coated on cotton fabrics characteristics and the results of the self-cleaning activity test of TiO₂ coated fabrics with citric acid binders were explained.

A. Characteristic of TiO₂ Nanoparticles Coated on Cotton Fabrics

The characteristic of fabric coated with TiO₂ and binder were studied on its stiffness properties and also elemental analysis of coated fabrics using EDX. The stiffness test result of coated cotton fabrics were showed in Table 1. The stiffcotton fabrics coated with TiO₂ nanoparticles and TiO₂ with binder were not change significantly for all variated binder composition. The stiffness value of cotton fabrics coated with binder greater than TiO₂ coated only. This indicated that crosslinking between cellulose and TiO₂ through esterification process increasing the number of group which bonded into cellulose producing stiffness.

TABLE 1. STIFFNESS VALUE OF COATED FABRICS

Fabrics	Stiffness (mg/cm ²)
Cotton fabric	3,7340
TiO ₂ coated cotton	5,2292
TiO ₂ -citric acid 25 g/L coated cotton	6,6247
TiO ₂ -citric acid 30 g/L coated cotton	4,9529
TiO ₂ -citric acid 35 g/L coated cotton	4,7118
TiO ₂ -citric acid 40 g/L coated cotton	5,5684

From EDX analysis, it can be confirmed the effect of the addition of citric acid binders can increase the nanoparticles of TiO₂ that are carried by electrostatic interactions between carboxylic anions of oxalic acid with Ti from TiO₂ under acidic conditions. The amount of Ti embodied in cotton fabrics supported by the results of EDX can be seen in Table 2. The number of Ti element embodied in TiO₂ cloth without binder has a weight percentage of 0.36% while on TiO₂ fabric with binder has a weight percentage of 0.9%. This result proved that binders can indeed increase the amount of Ti carried by electrostatic interactions between the carboxylic anion citric acid and Ti of TiO₂ under acidic conditions.

TABLE 2. EDX ANALYSIS OF COATED FABRICS

Elemen	TiO ₂ coated cotton		TiO ₂ -citric acid coated cotton	
	Wt %	At %	Wt %	At%
C K	35,65	44,30	34,16	43,15
OK	55,21	52,87	56,41	53,50
CoL	07,20	01,87	01,52	01,52
SiK	01,45	00,79	00,92	00,50
TiK	00,49	00,18	00,81	00,26
NaK	-	-	00,88	00,58
MgK	-	-	00,39	00,24
P K	-	-	00,51	00,25

B. Self Cleaning Activity Test Results

To see the ability of color stain degradation or self cleaning needs to be converted by means of the K / S value of the control fabric minus the K / S value of the coated fabric. The control was a cotton fabrics without TiO₂ or citric acid binder but still treated the same as two drops of 4R Ponceau stain and irradiated with 15 Watt UV for 5 hours. The absence of TiO₂ element in the control fabric, the K / S value obtained is the color aging which is only influenced by the degradation of UV lamps, knowing the effect of the UV lamp on the K / S value can then be used as a reduction on cotton cloth that has been coated with TiO₂ or binders with various concentration. The highest self cleaning activity of 3.03 was produced by cotton cloth coated with TiO₂ with 25% citric acid binder. The addition of binders has been shown to increase the self-cleaning ability of TiO₂-coated cotton cloth. The increased ability of self-cleaning was due to the amount of nano TiO₂ embedded in the fabric increases with the presence of oxalic acid binders. However, when the binder concentration was raised the self cleaning activity was decereas. It can be cause by the increase in binder concentrations above 25% make availability of the OH-group becomes more. The large number of OH-groups causes Ti to interact more and will carry more fabric. When Ti is carried a lot, this will cause the aggregation of nano Ti particles and then reduce the efficiency of photocatalyst work because the surface area is down [8].

TABLE 3. COLORING VALUE OF COATED FABRICS

Sample (R%)	K/S	
Cotton fabric	45,61	21,81596251
TiO ₂ coated cotton	13,56	5,816873156
TiO ₂ -citric acid 25 g/L coated cotton	7,94	3,032972292
TiO ₂ -citric acid 30 g/L coated cotton	29,67	13,85185204
TiO ₂ -citric acid 35 g/L coated cotton	13,33	5,702509377
TiO ₂ -citric acid 40 g/L coated cotton	8,61	3,363072009

V. CONCLUSION

Based on the results of research and discussion that has been done, it can be concluded as follows:

1. The result of self-cleaning activity test of cotton cloth coated with TiO₂ with 25% oxalic acid binder has better self cleaning activity than TiO₂ coated cotton cloth without using binder.
2. The results of elemental analysis of the fabric with EDX showed that the use of citric acid binder generate more Ti content on cotton fabrics, while the result of stiffness test showed there were no significant differences of TiO₂ coated cotton stiffness compared with TiO₂-binder coated cotton.

REFERENCES

- [1] Y. H. Lu, H. Lin, Y. Y. Chen, C. Wang, Y. R. Hua, "Structure and performance of bombyx mori silk modified with nano-TiO₂ and chitosan," *Fibers and Polimers*, vol. 8 (1), pp.1-6, 2007.
- [2] Y. Rilda, S. Fadhlil, A. Alif, A. Hermansyah, S. Chandren, N. Hadi, "Self-Cleaning TiO₂-SiO₂ Clusters on Cotton Textile Prepared by Dip- Spin Coating Process", *J. Tech. Eng.*, 2016.
- [3] D. R. Eddy, M. W. Lestari, I. Hestiawan, A. R. Noviyanti, "Sintesis Partikel Nano Titanium Dioksida pada Kain Katun dan Aplikasinya Sebagai Material Self- Cleaning," *Chemica et Natura Acta*, vol. 4 (3), pp.130-137, 2016.
- [4] J. Tian, L. Chen, Y. Yin, X. Wang, J. Dai, Z. Zhu, X. Liu, W. Pingwei, "Photocatalyst Of TiO₂/ ZnO Nano Composite Film: Preparation, Characterization, and Photodegradation Activity Of Methyl Orange," *Surface and Coatings Technol.*, vol. 204(1-2), pp.205-214, 2009.
- [5] C. Nasr, K. Vinodgopal, L. Fisher, S. Hotchandani, A. K. Chattopadhyay, and P. V. Kamat, "Enviromental Photochemistry on Semiconductor Surface. Visible Light Induced Degradation of a Textile Diazo Dye, Naphthol Blue Black on TiO₂ Nanoparticles," *J. Phys. Chem.*, vol.100, pp.8436-8442, 1999.
- [6] K. T. Meilert, D. Laub, J. Kiwi, "Photocatalytic self-cleaning of modified cotton textiles by TiO₂ clusters attached by chemical spacers", vol.237, *J. Mol. Catalysis A: Chemical*, 2005, pp.101-108.
- [7] K. Karimi, L. Loghan, M. Mirjalilii, M. E. Yazdanshenas, A. Nazari, Effect of Nano TiO₂ on self Cleaning Property of Cross Linking Cotton Fabric with Succinic Acid Under UV Irradiation, Textile Department, Islamic Azad University, Yazd Branch, Yazd, Iran, in press.
- [8] H. Hashemikia and M. Montazer, Sodium hypophosphite and nano TiO₂ inorganic catalysts along with citric acid on textile producing multi- functional properties, Elsevier, 2012.
- [9] B. Mahltig, H. Bottcher, and H. Helfried, "Functionalization of Textiles by Inorganic Sol-Gel Coatings," *J. Mater. Chem.*, vol.15, pp.4385-4398, 2005.