SILK FABRICS COATED ZnO NANOPARTICLES AND DYEING WITH NATURAL INDIGO TO ENHANCE FUNCTIONAL TEXTILES

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Abstract

Silk fabrics are modified by dyeing with natural indigo and ZnO nanoparticles coating to enhance functional textiles. Silk fabrics are coated with different weight of 1, 2, 3, and 4 g of ZnO nanoparticles. The properties of coated silk fabrics and color fastness of fabrics dyed were investigated. The FE-SEM and EDS results of the coated silk with ZnO nanoparticles were clearly confirmed the strongly adsorption bond of ZnO on the surface of silk adsorbent. Silk coated 3 g ZnO nanoparticles also provide optimal condition as the presence of Zn content on silk surface remain contain approximately 79.00, 76.84, and 75.95 wt%, which was slightly decreased after repeated 10, 20 and 30 washed cycles, respectively. Coated silk fabrics samples and indigo dyed exhibited excellent anti UV protection with UPF values in the range of 49.31 to 105.83. ZnO nanoparticles modified silk fabrics can be used for improved washing fastness of natural indigo dyed, UV protection, heat resistant, color fastness and durability of antibacterial.

Keywords: **Silk fabric, Zinc oxide nanoparticle, Indigo, UV protection, Antibacterial, Color fastness**

Introduction

For millennia, numerous Asean countries such as India, Japan, Thailand, and Southeast Asian nations have used indigo as a dye. Indigo is now used as a dye for fabrics such as cotton, silk, wool, and leather. It is also used as a dye for sketching and printing. *Indigofera tinctoria* is the principal commercial indigo species in Thailand. Indigo's chemical formula is $C_{16}H_{10}N_2O_2$. Indigo pigment is not water soluble. Therefore, the indigo molecule has to be first converted into a water soluble form, and then indigo dye is converted via a reduction reaction to the colorless and water-soluble leucoindigo or indigo white. Indigo reduction can be prepared in many ways, such as reducing with sodium dithionite or sodium hydrosulphite, ($Na_2S_2O_4$) (Hossain *et al*., 2017), sodium hydroxide (NaOH) (Kongkachuichay *et al*., 2010), thiourea dioxide ($CH_4N_2O_2S$) and natural reducing sugar (Blackburn and Harvey, 2004; Ticha *et al*., 2013; Shin *et al*., 2014; Saikhao *et al*., 2018). The most common reducing agent for industrial indigo dyeing process is sodium dithionite ($Na_2S_2O_4$), which can generate sulfite and sulfate into wastewater (Saikhao *et al*., 2018). According to environment causes various problems and the carcinogenic effects (Adeel *et al*., 2022), to human so many researchers have attempted to look for green technologies in all textile industry processes (Adeel

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et al., 2020) as isolation and extraction (Adeel *et al*., 2021), natural dyes material (Habib *et al*., 2021), (Kiran *et al*., 2020), bio-mordants (Zuber *et al*., 2020) and natural reducing agent. Natural reducing agent as reducing sugars that can replace chemical reducing agents for dyeing vat indigo dye. Reducing sugars in sulfur dyeing could provide a sustainable, nontoxic, biodegradable, cost-effective. Many fruits are high in naturally sugar as glucose, fructose and sucrose. These high sugar materials assure that the indigo vat will go into reduction quickly and successfully (Ellis, 2020). Different kinds and parts of fruits, palm, apple, banana (Hossain *et al*., 2017), ripe banana (Lasopha *et al*., 2015), banana peel (Shin *et al*., 2013) and bokbunja (Rubus coreanus Miq.) sludge (Shin *et al*., 2014), pineapple, water melon, star fruit and tamarind (Tangkawanit, 2020) were applied as reducing agents in the indigo dyeing process. Glucose also could effectively reduce the indigo dye in the natural indigo dyeing process (Ticha *et al*., 2013; Shin *et al*., 2016; Saikhao *et al*., 2017).

Tamarind pulp is also a rich source of sugars and an excellent source of B-vitamins and exhibits high antioxidant capacity that appears to be associated with a high phenolic content (Almeida *et al*., 2009). The percentage of the constituents contains tartaric acid ranging from 8-18%, reducing sugars 25-45%, pectin 2-3.5% and protein 2-3% (Obulesu *et al*., 2011). Therefore, tamarind pulp was used as a reducing agent in indigo dyeing processes for this study.

Ultraviolet (UV) rays from the sun is well known to be associated with various skin cancers, accelerated skin aging, cataract (opacity in the lens of the eye) and other eye diseases, and possibly an adverse effect on a person's ability to resist infectious diseases (Belkin *et al*., 2020). The nanomaterial properties can be increased the physical properties of fibers including anti-fungal and bacterial, waterproof, dirt, crease, UV resistance, fire resistance. Moreover, it can increase color fastness and tensile strength in textile (Yadav *et al*., 2006). Zinc Oxide (ZnO) has already been studied to improve surface modification, self-cleaning, purification, antimicrobial and UV-protective agents, flame retardancy and thermal stability, moisture management, hydrophobicity, electrical conductivity (Verbič *et al*., 2019), photocatalytic (Moradi *et al*., 2016), improved mould-resistance (Li *et al*., 2017) and sensor (Dang *et al*., 2019). ZnO's composites on silk fabrics also showed performance and efficiency in advanced protective textiles, self-cleaning fields and exhibited excellent anti-UV protection with UPF value over 50 (Huang *et al*., 2019). The ZnO nanoparticles and protein sericin showed good antimicrobial properties for both *Staphylococcus aureus* and *Escherichia coli* (Kiro *et al*., 2017). The UV protection mechanism of ZnO involves the absorption of UV radiation as well as the refraction and/or scattering of the UV rays through its high refractive index, which directly prevents and diffuse transmittance of UV rays through textile material to reach the skin. Coating processes on textiles such as dip-coating, sol-gel, padding, electro deposition, cross link and chemical bath deposition are usually performed (Verbič *et al*., 2019). Zinc oxide coated on cotton has been reported at various methods such as microwave method, pad dry cure, immerse and cross link have an effect on UV protection properties (Yadav *et al*., 2006; AbdElhady, 2012; Sundrarajan *et al*., 2012; Shaheen *et al*., 2016; Wang *et al*., 2016a; Thi and Lee, 2017; Tangkawanit, 2020). ZnO nanoparticles were also coated on silk fiber had significant improvement in tensile strength and excellent on antimicrobial activity (Gram-positive and Gram-negative) and fungi (Kiro *et al*., 2017; Dang *et al*., 2019; Shubha *et al*., 2019). It was also observed that ZnO particle can increase in fiber hydrophilicity and surface roughness enhanced the amount of adsorbed ZnO particles, reflecting higher antimicrobial activity (Toboła *et al*., 2018). Nanoparticles can provide high durability for treated fabrics due to large surface area and high surface energy that ensure better affinity for fabrics and lead to an increase in durability of the textile functions (Vigneshwaran *et al*., 2006; Yadav *et al*., 2006). ZnO nanoparticles were applied to cotton and wool samples to impart sunscreen activity to the treated textiles (Becheri *et al*., 2008). Coating processes of ZnO nanoparticles on silk fabrics for this work was used cross link method (Karimi *et al*., 2010).

The purpose of this research was to investigate physical properties of silk fabrics coated with ZnO nanoparticles and natural indigo dyed. The effect of ZnO nanoparticle modified on silk fabrics both before and after dyed as UV protection, thermal properties, tensile strength, air permeability, vertical resistance, color fastness, coating durability and also washing fastness of antibacterial were reported. The proposed schematic mechanism of ZnO nanoparticles coated on silk fabric dyed with natural indigo (a) and functional textiles (b) shows in Figure 1. The cross-linked silk was binded the H-bond between the amine groups of the silk and the carboxylic acid group of the cross link. The ZnO nanoparticle was coated by the remaining carboxylic acid groups chelated with ZnO. For, indigo dye, the carbonyl groups of indigo and amine groups of protein were chelated with ZnO.

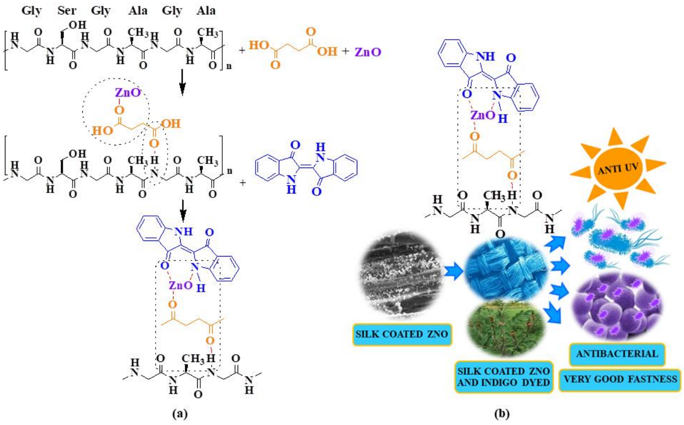

Figure 1. Proposed schematic mechanism of ZnO nanoparticles coated on silk fabric dyed with natural indigo (a) and functional textiles (b)

Materials and Methods

Materials

Warp and weft silk yarn used in weaving was supplied as ready to be used from Chul Thai Silk Co., Ltd, Amphoe Muang Phetchabun, Phetchabun, Thailand. Silk fabric was plain weave. Silk fabrics were cleaned again by soaking into nonionic detergent at room temperature for 24 h. The silk was washed and air-dried. ZnO nanoparticles was purchased from Infarmat Product Company #30N-0801 Nano ZnO Powder, 99.7%, particle size 30 nm, m.p. 1,980°C, density 5.6 g/cm^3. Succinic acid $(CH_2COOH)_2$ as a cross-link agent was purchased from Ajax Finechem, Australia, (Analytical grade). Sodium hypophosphate (NaH_2PO_4) as a catalyst was purchased from Ajax Finechem, Australia, (Analytical grade). The commercial available natural indigo was extracted from *Indigofera tinctoria*, obtained from Sakon Nakhon province, Thailand. Natural reducing agent as Tamarind was collected from a local market, Ubon Ratchathani province, Thailand.

Cross-Link Agent Preparation and Cross-Link Agent Coated

Succinic acid $(CH_2COOH)_2$ 6% (wt/wt) in the presence of sodium hypophosphate (NaH_2PO_4) 4% (wt/wt) was performed by weighted 40 g of sodium hypophosphate dissolved into 1,000 mL deionized water. 60 g succinic acid was combined with 940 g sodium hypophosphate, stirred, and stored for subsequent research. Silk textiles were cut into 10x10 cm^2 squares and precisely weighed, then soaked in deionized water and heated 1 h at 80°C to remove wax and impurities. In a 250 mL baker, 100 mL of cross-link agent solution was added. Silk samples were immersed in an aqueous solution of cross-link agent for 1 h. Cured silk fabrics were dried in an oven at 85°C for 3 min and then applied to continuous curing at 180°C for 2 min, allowed to air dried at room temperature for 24 h (Karimi *et al*., 2010).

Coated Silk Fabrics with ZnO Nanoparticles

1, 2, 3, and 4 g ZnO nanoparticles were weighted, then 100 mL deionized water was added, stirred with a glass rod, and sonicated the respective ZnO nanoparticle suspensions for 1 h. Silk fabrics coated with cross-link agent were immersed into the ZnO nanoparticles suspension, then heated in constant water bath at 80°C for 1 h The coated silk was cured in an air oven at 100°C for 30 min to fixed ZnO nanoparticles on the fabric. Cured fabric was sonicated for 10 min to remove nonbonding reaction of ZnO nanoparticles on silk fabric, it was allowed to air dry at ambient temperature for 24 h (Karimi *et al*., 2010).

Characterization

Morphology of uncoated silk and silk coated with ZnO nanoparticles was analyzed by using the scanning electron microscope (SEM), model JSM-6010LV, JEOL, USA. The UV resistance was also confirmed by using the UV-visible spectrophotometer (UV), Lambda 35, Perkin Elemer Company, USA. Thermal resistance was carried out using a Thermogravimetric analysis (TGA) METTLER Toledo, Model TGA/DSC1, USA, instrument with nitrogen as the purging gas in a temperature range of 25-1,000°C. Rate 10°C/min. The crystallinity of the ZnO, silk, indigo and silk coated ZnO and indigo dyed was determined using an X-Ray Diffractometer, Bruker, Model D8 advance, Germany with Cu Kα (λ=1.54060) radiation. The difractrograms were obtained in 2θ range from 10 to 80°C, 40 kV, 40 mA. The functional group of the silk fabrics, ZnO nanoparticles and indigo were determined in the wavenumber range between 4000 and 400 cm^{-1} by using a Attenuated Total Reflectance-Fourier Transform Infrared spectrophotometer (ATR-FT-IR), Model 45321 Spectrum 2000, Perkin Elemer Company, USA. The elemental analysis of ZnO nanoparticles coated on silk and washing fastness for 10, 20, and 30 washed cycles was confirmed by using Energy-dispersive X-ray Spectrometer (EDS) analysis, which is an attachment to the Field Emission Scanning Electron Microscope (FE-SEM-EDS), Carl Zeiss Model Auriga. Germany, Oxford. Hence, the silk fabrics coated 3 g ZnO nanoparticles was selected to be studied further for modified silk fabrics and indigo dyed.

Preparation of Indigo Vat and Silk Dyed

1 kilogram of indigo paste was mixed with 1 liter of warm (40°C) alkali wood solution pH 9 to 11. Tamarind 100 g was mixed with 1 liter warm water at 40°C. The indigo vat reaction was mixed together and continuous stirred for 5 min, then left at room temperature for 24 h. Silk fabrics coated with ZnO nanoparticles were soaked in deionized water for 1 h, dyed with indigo for 5 min, and then allowed to be oxidized with oxygen in the air for 3-5 min, duplicated for 6 times, washed until neutral pH and air dried at room temperature.

Physical Properties of Silk Fabrics Testing

The dyed silk fabrics were measured the color strength by using the Chroma meter for the K/S, L*, a* and b* values. Morphology of silk coated with ZnO nanoparticles was analyzed by the scanning electron microscope (SEM), model JSM-6010LV, JEOL, USA. The light fastness was measured according to ISO 105-BO2: 1994 (E), washing fastness was measured according to TISI 121, Volume 3: 2009 Method A (1) (40°C, 30 min). The washing fastness of nano materials washed for 10, 20, and 30 cycles was carried out and the UV resistance was also confirmed by using the UV-visible spectrophotometer (UV), Lambda 35, Perkin Elmer Company, USA.

The Mechanical Properties Testing

The mechanical properties of silk coated with ZnO nanoparticles, such as tensile strength (Mpa) was measured by tensile testing machine (Instron model 5566), according to ISO 13934-2: 1999(E) standard, condition testing: temperature 20±2°C, relative humidity 65±4%. The air permeability was evaluated with a M021A air permeability tester. Standard method was used to measure the pressure difference between two surfaces (100 Pa), area testing of 20 cm^2 (ISO 9237: 1995 (E)). The vertical resistance was measured by a static lab tester (Mesdan Lab Code 291 B), air temperature = 23±1°C, relative humidity = 25±5%, according to standard testing of BS EN 1149-1: 2006.

Measurements of Antimicrobial Activity

The antimicrobial activity of uncoated silk and silk coated with ZnO nanoparticles was evaluated by using standard method according to the AATCC TM147. *Staphylococcus aureus* (gram-positive bacteria) *and Escherichia coli* (gram-negative bacteria) were cultivated in trypticcase soy broth (TSB), liquid incubator for 200 cycles per min at 37°C for 24 h. Silk fabric specimens are placed in intimate contact with agar surface, after that incubated 37°C for 24 h. The formation of clear rings was observed around the silk fabric sample, triplicate testing per sample.

Results and Discussion

Characterization of ZnO Nanoparticles and Coated Silk Fabrics

The surface morphology of uncoated and coated silk sample with ZnO nanopaticles was investigated by SEM image. Figure 2 shows the SEM images of (a) uncoated silk, (b) ZnO, (c-f) silk coated with various amount ZnO nanopaticles. It was also seen that the ZnO nanoparticles were well dispersed on surface of the coated silk fabrics sample. The uncoated silk had a relatively smooth surface as shown in Figure 2(a) while treated silk fabric morphology had a rougher surface that covered with a very small nanoparticles of ZnO (Figure 2(c)-(f)). The much rougher surface due to facilitate the deposition of more ZnO nanoparticles on silk fabric that were also increased the dispersion with increasing concentration of ZnO treatment (Wang *et al*., 2016a). These images helped to confirm the dispersion of ZnO nanoparticles on the surface of silk fabric samples.

Thermal Resistance

The TGA curves of silk, ZnO, silk coated with 3 g ZnO and silk coated with 4 g ZnO nanoparticles with a heating rate 10 K/min were presented in Figure 3. A little weight loss of ZnO in a temperature range of 25-1,000°C was about 1.50%, residual weight 98.50%. The initial weight loss of silk, silk coated with 3 g ZnO and silk coated with 4 g ZnO was about 6% until 200°C. These weight loss could be attributed to the elimination of adsorbed water. Silk fibroin was hydrophilic, so a dehydration process of adsorbed or crystal water was released (Feng *et al*., 2006). The weight loss of uncoated silk about 70.39%, silk coated 3 g ZnO about 66.37% and silk coated 4 g ZnO about 61.14% for the took place in a temperature range of 200-600°C which should be associated with the breakdown of side chain groups of amino acid residues as well as the cleavage of the peptide bonds (Nogueira *et al*., 2010; Ranjana *et al*., 2020). As the thermal properties of uncoated silk reflected weight loss higher than silk fabrics coated with ZnO nanopaticles.Weight loss of uncoated silk about 80%, silk coated 3 g ZnO about 75% and silk coated 4 g ZnO about 70% in a temperature range of 600-850°C**,** the extra stability heat resistance could be attributed to the bondage between the silk fabrics and ZnO nanoparticles (Ranjana *et al*., 2020).

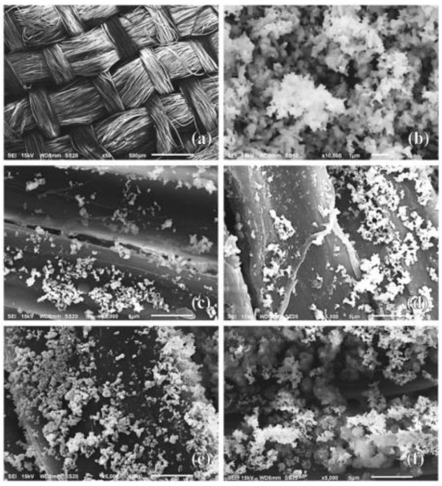

Figure 2. SEM images of (a) uncoated silk, (b) ZnO, (c) silk coated 1 g ZnO, (d) silk coated 2 g ZnO, (e) silk coated 3 g ZnO, and (f) silk coated 4 g ZnO nanoparticles

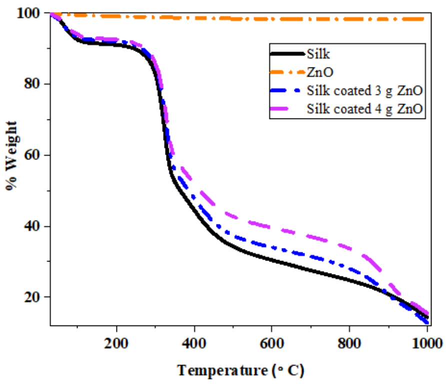

Figure 3. TGA curves of uncoated silk, ZnO, silk coated 3 g ZnO and silk coated 4 g ZnO nanoparticles

The Mechanical Properties

Table 1. shows tensile strength, vertical resistance and air permeability values of uncoated and silk fabrics coated ZnO nanoparticles. Tensile strength of uncoated silk both longitudinal yarn (1.62×10^{-4} MPa) and streaking of yarn (4.92×10^{-4} Mpa) was higher than that of coated silk for longitudinal (1.49×10^{-4} Mpa) and streaking of yarn (4.60×10^{-4} Mpa). The results showed that tensile strength value was significantly decreased which was in good agreement with Shaheen *et al.* (2016); Garrido *et al.* (2020). The tensile strength of silk fibroin (0.41±0.12 MPa) was higher than that of silk fibroin coated ZnO nanoparticles (0.32±0.10 MPa). The deposition of ZnO also gave rise to a significant decrease in the diameter of the fibers. Silk fibroin was estimated around 2,948±748 nm and silk fibroin coated ZnO was 2,766±599 nm. The tensile strength of untreated cotton fabric was 6.1782 MPa and for treated cotton fabric decreased to 6.0801 MPa and 5.9919 MPa when the concentration of ZnO nanoparticles was 2 g and 3 g, respectively. Shaheen *et al.* (2016) have reported that coated ZnO nanoparticles on cotton fabric does not cause any significant damage to the structure of cotton, which confirmed with elongation to auto break increased with increasing the concentration of ZnO nanoparticles. Elastic Modulus was also decrease for silk fibroin, 24.24±8.13 MPa and silk fibroin coated ZnO, 20.77±10.21 nm (Garrido *et al*., 2020). Vertical resistance of uncoated silk fabrics was also decreased when compared to silk fabrics coated with 3 g ZnO nanoparticles for both surface resistivity and surface resistant.

Air permeability of uncoated silk was 49.58 cm^3/sec./cm^2 and silk coated ZnO nanoparticles 3 g was 41.56 cm^3/sec./cm^2. The air permeability of silk decreased after treated with ZnO nanoparticles. This phenomenon was corresponding to previous research by Farouk *et al*. (2012). Air permeability is an important factor in the performance of textile materials used to give an indication to the breathability of the coated fabrics. The air permeability value in uncoated cotton fabrics was found to be 250.5 l/dm^2.min and cotton treated with ZnO sol/chitosan was 243.2 l/dm^2.min. As can be seen, a modest drop may be attributed to the closure of open interstices generated by the finish's mechanical deposition (Karolia *et al*., 2007; Farouk *et al*., 2012).

Table 1. Tensile strength, vertical resistance and air permeability values of uncoated and silk fabrics coated ZnO nanoparticles

Samples	Tensile strength (MPa)		Vertical resistance (Ohm)		Air permeability (Cm^3/sec./Cm^2)
	Longitudinal yarn	Streaking of yarn	Surface resistivity	Surface resistant	
Uncoated silk	1.62×10^{-4}	9.20×10^{-4}	8.4×10^{12}	4.2×10^{11}	49.58
Silk coated 3 g ZnO	1.49×10^{-4}	4.60×10^{-4}	7.6×10^{12}	3.8×10^{11}	41.56

Washing Durability

The element composition of uncoated silk fabric and silk coated with 3 g ZnO nanoparticles after 10, 20, and 30 washed cycles were demonstrated by FE-SEM-EDS, as shown in Figure 4. The FE-SEM and EDS results of the coated silk with ZnO nanoparticles were clearly confirmed the strongly adsorption bond of ZnO on the surface of silk adsorbent. Zn and O elements were detected in the EDS spectrum. Uncoated silk contained C and O of 78.71 and 21.29 wt%, respectively, without Zn element content. The EDS elemental analysis for durability of 3 g ZnO nanoparticles coated silk fabrics were decreased which affected by repeating 10, 20, and 30 washed cycles (Figure 4). Uncoated silk EDX spectrum shows the presence of C and O element indicating the purity of the control silk sample. After coated silk with ZnO nanoparticles, EDS analysis showed the presence of Zn with C and O in the sample supporting the elemental mapping. Silk surface composition remaim approxymately 79.00, 76.84 and 75.95 wt% ZnO nanoparticles, which was slightly decreased after repeated 10, 20 and 30 washed cycles, respectively.

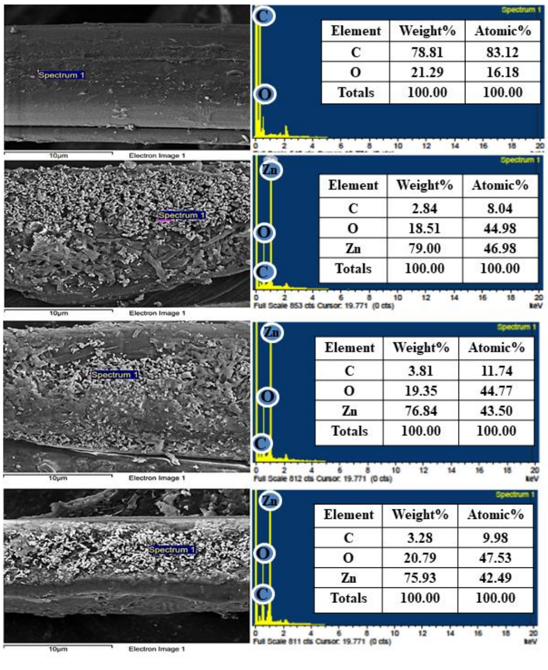

Figure 4. FE-SEM and EDS elemental analysis of a) uncoated silk and coated silk fabrics with 3 g ZnO nanoparticles b) 10 washed, c) 20 washed and d) 30 washed cycles

Antibacterial Property

Table 2 showes *Staphylococus aureus* and *Escherichia coli* reduction of silk fabrics coated 1, 2, 3, and 4 g of ZnO nanoparticles. It was also observed that the antibacterial property of *Escherichia coli* (gram-negative) was greater than that of *Staphylococus aureus* (gram-positive). The cytotoxicity of ZnO nanoparticles depends on both size and concentration. The antibacterial efficiency of ZnO particles showed that at lower concentrations of ZnO were more effective against gram-positive than gram-negative bacteria. The gram-positive bacteria have a much thicker cell wall peptidoglycan compared to gram-negative bacteria, which results in a decreased susceptibility to the membrane damage induced by ZnO particles (Fiedot *et al.*, 2017; Verbič *et al.*, 2019). Silk textiles treated with 3 g of ZnO nanoparticles demonstrated the largest percent reduction of *Escherichia coli*, reaching a value of 97.78. Antibacterial properties of silk fabrics coated ZnO nanoparticles after 10, 20, and 30 washed cycles against both *Staphylococus aureus* and *Escherichia coli* bacteria expressed as percent reduction. The bacteria reduction of untreated silk fabrics was zero exhibited a properties against both types of bacteria. The durability of the antibacterial properties coated silk with 3 g of ZnO nanoparticle was decreased which affected by repeating 10, 20, and 30 washed cycles. Coated silk fabrics demonstrated that the durability of the antibacterial properties against 30 washed cycles of 21.69 and 20.81 for *Staphylococus aureus and Escherichia coli*, respectively. ZnO had affected to bacterial on finished silk fabrics due to free an electrons (e^-) generated and the holes (h^+) with positive charge when ZnO nanoparticles were exposed to Uv radiation. The active oxygen that activated by the holes can be oxidized microorganisms. ZnO has a positive charge that can interact with the molecular groups with negative charges (electrostatic force) on the bacteria cell surface (Grifoni *et al.*, 2014). The results assumed that ZnO nanoparticles could be good antibacterial material of the finished silk fabric. Nanoparticles also can provide high durability for treated fabrics as they have large surface area and high surface energy to increased affinity for fabric and lead to increase in the durability of textile functions (Vigneshwaran *et al.*, 2006; Yadav *et al.*, 2006; Wang *et al.*, 2016b; Alebeid *et al.*, 2017)

Table 2. FE-SEM and EDS elemental analysis of a) uncoated silk and coated silk fabrics with 3 g ZnO nanoparticles b) 10 washed, c) 20 washed and d) 30 washed cycles

Samples	Reduction percent of *S.aureus*	Reduction percent of *E.coli*
Uncoated silk	0	0
Silk coated 1 g ZnO	87.921	95.963
Silk coated 2 g ZnO	74.438	97.211
Silk coated 3 g ZnO	82.022	97.780
Silk coated 4 g ZnO	77.247	96.385
Silk coated 3 g ZnO 10 washed	66.038	58.947
Silk coated 3 g ZnO 20 washed	50.130	41.821
Silk coated 3 g ZnO 30 washed	21.698	20.817

Color Shade and Color Strength

Color shade of uncoated silk (row 1) and silk coated with 3 g ZnO (row 2) and dyed with indigo for various number dips shown in Figure 5. Color shade of silk dyed with indigo has appreciable effected on number dips. It is evident that color shade slightly change from light blue to dark blue when the silk was dyed from 1 dip to 6 dips. The colorimetric data of uncoated (u) silk and indigo dyed reflected that K/S_u values increases as the number dips increases due to indigo molecules adsorbed on silk increases. The a^*_u and b^*_u value was also slightly increased consistency with the number dips increased, and the highest color strength was 6 dips. Color strength (K/S) and color coordinates, L^*, a^*, and b^* values of silk coated with ZnO nanoparticles and indigo dyed showed in Figure 6. The enhancement in the color depth of dyeing caused by the present of indigo dye molecules complex with ZnO coated on the silk surface corresponding to the brightness or L^* value decrease and lead to more adsorption of dye molecules on the silk fabrics. Coated silk samples showed higer K/S values as compared to uncoated silk under the same dip. Higher K/S values indicated higher adsorption of indigo dyed and deeper colors due to higher surface area of coated silk with ZnO nanoparticles and also increase UPF values (Sarkar, 2004; Erkan *et al.*, 2014).

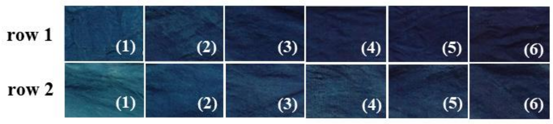

Figure 5. Color shade of uncoated silk (row 1) and silk coated with 3 g ZnO (row 2) and dyed with indigo for various number dips as 1, 2, 3, 4, 5 and 6 dips

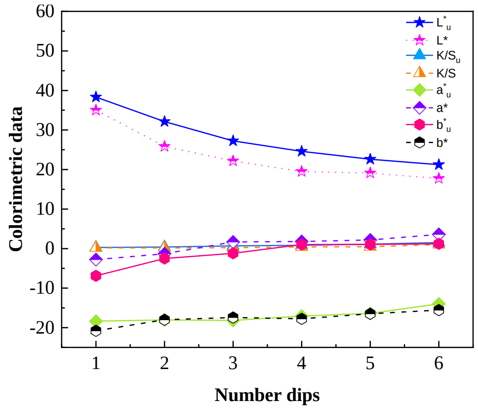

Figure 6. Colorimetric data of uncoated silk and silk coated with 3 g of ZnO nanoparticles and indigo dyed for various number dips as (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 and (f) 6 dips

XRD Patterns Characterization

The XRD patterns of ZnO nanoparticle exhibited the peaks attributed to hexagonal system. The pattern of the characteristic peaks at 2θ diffraction angles of 32, 34, 36, 47, 57, 63, 66, 68, 69, 72, and 77, corresponding to the planes 100, 002, 101, 102, 110, 103, 200, 212, 201, 004, and 002 respectively, were clearly observed (JCPDS card no. 36-1451) (Garrido *et al.*, 2020). XRD peaks of silk fibroin were associated with its crystalline structure domain at around 2θ equal 20.64 (Su *et al.*, 2011). The XRD analysis of natural *indigofera tinctoria* powder revealed the presence of crystal peaks at different angles at 11.98, 13.69, 16.60, 20.28, 29.21, 31.57, 34.20, 47.29, 56.42, 62.62, 67.80, and 68.48 2θ which did not found in the JCPDS library. However, silk coated with ZnO nanoparticle and indigo dyed showed all main distinct Bragg reflections matching with XRD patterns of the raw ZnO, silk and indigo which confirmed the resulting in good coating and dyeing method (Figure 7).

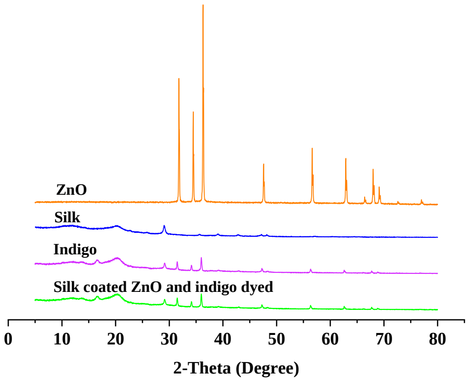

Figure 7. XRD patterns of ZnO, silk, indigo and silk coated ZnO and indigo dyed

ATR-FT-IR Characterization

ATR-FT-IR spectra of uncoated silk, indigo, uncoated silk dyed with indigo and coated silk dyed with indigo shown in Figure 8. The ATR-FT-IR spectrum of uncoated silk fabrics shows a broad peak at 3278 cm^{-1} corresponding to N-H stretching and a peak at 1622 cm^{-1}, 1511 cm^{-1} and 1227 cm^{-1} were ascribed to the stretching vibration of amine I, amine II and amine III, respectively. (Nogueira *et al*., 2010; Dayioglua *et al*., 2015; Chitichotpanya and Chitichotpanya, 2017). The absorption band of indigo at 3263 cm^{-1} corresponds to the excitation of N-H bond and the peak near 1612 cm^{-1}corresponds to the C=O bond while the strong peak at 1395 cm^{-1} corresponds with the N-H (rocking) and C-N (stretching) (Baran *et al*., 2010). The absorption peak ranging from 400 cm^{-1}- 500 cm^{-1} was attributed to the characteristic stretching mode of Zn-O bond (Nagaraju *et al*., 2010).

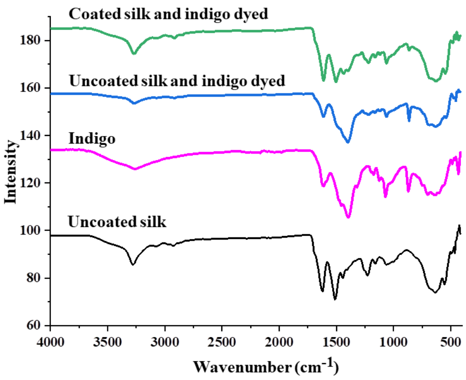

Figure 8. ATR-FT-IR spectra of uncoated silk, indigo, uncoated silk dyed with indigo and coated silk dyed with indigo

Color Fastness

Fastness properties comparision of uncoated silk and silk fabric coated with various concentrations of ZnO nanoparticles and indigo dyed were shown in Table 3. Uncoated silk fabrics dyed with indigo reflected good light fastness. All coated silk fabrics dyed with indigo showing good to very good (4-5) light fastness. Washing fastness of uncoated silk was found to be in the range of 3-4 (moderate to good). Silk fabric coated with ZnO nanoparticles had been increased washing fastness rating of 4-5 (good to very good). The result reflected that washing fastness value of coated silk fabrics with ZnO nanoparticles was increasing to very good (5) rating when increased 2 to 4 g ZnO nanoparticles concentration because of ZnO nanoparticles increasing surface area to adsorbed indigo dyed molecules.

UV Protection

Table 4 shows the percentage UVA and UVB radiation and UPF value of the uncoated silk and silk fabric samples coated with 1, 2, 3, and 4 g ZnO nanoparticles. The UPF value of uncoated silk fabrics and indigo dyed was very good (UPF 35.60). Indigo dye structure contained the multi-graded band gap that enhanced the light absorption and can make the indigo material to be used in solar cell and optoelectronic applications. Indigo has anticancer and antibacterial effects. It is also effective in eliminating toxic substance, dispelling heat and dampness diminishing inframmation and relieving pain (Bouzidi *et al*., 2017). The UPF values of 1, 2, 3, and 4 g of ZnO coated silk fabrics samples and indigo dyed were excellent as high as 48.31, 50.71, 100.06, and 105.83, respectively (Grifoni *et al*., 2014). When the percentage depth of shade was increased, the UPF values increased so darker color as indigo (blue), navy blues, black and dark green which can provide better protection with higher UV adsorption (Sarkar, 2004; Grifoni *et al*., 2009). The ZnO concentration on coated silk fabrics is directly influenced by UPF protection values ZnO nanoparticles. ZnO has excellent effectiveness in blocking both UVA and UVB radiation (Dang *et al*., 2019). ZnO composites on silk fabrics also showed efficiency to protective textiles and exhibited excellent anti-UV protection with UPF value over 50 (Huang *et al*., 2019). Nanoparticles have a larger surface area per unit mass and volume than that of the conventional materials, leading to the increase of the effectiveness of blocking UV radiation (Wong *et al*., 2006).

Table 3. Fastness properties comparision of uncoated silk and silk coated with various concentration of ZnO nanoparticles and natural indigo dyed

Samples	Light fastness	Washing fastness			
		c.c.	c.s.c.	c.s.s.	c.s.w.
Uncoated silk	4	3-4	4	4	4
Silk coated 1 g ZnO	4-5	4-5	4-5	4-5	4-5
Silk coated 2 g ZnO	4-5	5	5	5	5
Silk coated 3 g ZnO	4-5	5	5	5	5
Silk coated 4 g ZnO	4-5	5	5	5	5

c.c = color change; c.s.c. = color staining on coton; c.s.s. = color staining on silk; c.s.w. = color staining on wool.

Table 4. UPF protection values of silk fabrics coated with ZnO nanoparticles and natural indigo dyed

Samples	UVA (%)	UVB (%)	UPF	Protection category
Uncoated silk	2.76	2.96	35.60	Very good
Silk coated 1 g ZnO	2.04	2.19	48.31	Excellent
Silk coated 2 g ZnO	1.96	2.09	50.71	Excellent
Silk coated 3 g ZnO	0.98	1.04	100.06	Excellent
Silk coated 4 g ZnO	0.94	1.00	105.83	Excellent

Conclusions

ZnO nanoparticles modified on silk fabrics and natural indigo dyed could be improved thermal stability, Uv protection, color fastness, washing fastness of antibacterial properties. Silk fabrics coated with 3 g ZnO reflected the highest antibacterial. The FE-SEM and EDS have been used to confirm for good durable antibacterial both *Staphylococus aureus* and *Escherichia coli* after 10, 20, and 30 washed cycles. Silk fabrics modified the surface by using 2, 3, and 4 g ZnO nanoparticles and dyed with natural indigo had improved washing fastness to very good (5) rating. Silk fabrics coated with 3 g ZnO nanoparticles and indigo dyed also provide perfect conditions for UV protection and *Escherichia coli* reduction. This results indicated that ZnO nanoparticles is an effective material to modified the silk fabrics and natural indigo dyed for further textile application.

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