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THE EFFECT OF COMPOSITIONAL OPTICAL ANALYSIS OF ZnO/TiO_2 COMPOSITES IN A SUNSCREEN PRODUCT

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ABSTRACT

TiO_2 and ZnO are active components in commercialized physical sunscreens that have a broad protective spectrum, which includes UVB and UVA. The combination of ZnO/TiO_2 composites has more effective performance in blocking Ultra Violet rays in a wide wavelength range compared to ZnO or TiO_2 alone. However, the high refractive index of TiO_2 can cause a white cast. To solve the issue, a cream was created by incorporating antioxidants such as Virgin Coconut Oil (VCO). The purpose of this study is to determine the effect of the ZnO/TiO_2 composite optical composition on visible and ultra violet light. Three composition comparisons were investigated in the study: ZnO/TiO_2 10% added VCO, ZnO/TiO_2 5% added VCO, and ZnO/TiO_2 5% without VCO. UV-vis spectroscopy characterization showed that the ZnO/TiO_2 composite absorbed more effectively in the ultra violet range than in visible light, and the greatest absorption and maximum reflectance are in the UVA1 range. The higher the concentration of ZnO/TiO_2 in the cream composition, the higher the cream's absorption and reflection peaks. The reflectance in the visible light region is low, between 30% and 40%, implying that visible light passes through the sunscreen cream 70% to 80% of the time. As a result, the higher the ultra violet reflectance of the physical sunscreen cream, the lower the transparency. The higher the concentration of ZnO/TiO_2, the greater the band gap value of the physical sunscreen, in the range of 3.1–3.5 eV.

Keywords : Physical Sunscreen; Zink Oxide; Titanium Dioxide; Composites; Optical Properties

I. INTRODUCTION

The technological innovation of cosmetics improves in today's modern society, the function of sunscreen can be combined into cosmetics. Sunscreen has a significant contribution in satisfying our daily routine. In terms of health and aesthetics, sunscreen cosmetics are preferable to other cosmetic products in this modern era. The use of sunscreen is very necessary in the most exposed places, and often humans walk and drive in the sun, so the skin is always at risk from sun exposure and can even be attacked by diseases caused by ultraviolet radiation (UV) [1].

The UV radiation spectrum ranges from 100 nm to 400 nm, while the visible spectrum has wavelengths ranging from 400 nm to 800 nm [1]. Ultraviolet (UV) light is classified into three types based on its wavelength range, which is the UV-A radiation wavelength range of 320 nm to 400 nm. Furthermore, UVA wavelengths tend to be categorized as UVA2 wavelengths that stretch from 320 nm to 340 nm and UVA1 wavelengths ranging from 340 nm to 400 nm. These rays cause greater erythemogenic disease than UVA wavelengths, especially UVA2, and also cause photoaging, wrinkles, reduced skin elasticity, and malignant melanoma, a type of skin cancer associated with UV exposure [2]. Next is UVB, with a wavelength of 280 nm to 320 nm. These rays cause redness and hyperpigmentation of the skin. Finally, UVC has a wavelength of 280 to 320 nm [3]. These light rays do not reach the earth's surface. A possible solution to the efforts made to avoid negative impacts on the skin is to use sunscreen.

Sunscreen is a type of cosmetic that can be used as a skin care product to shield the skin from the damaging impact of exposure to sunlight [4]. Sunscreen should protect people from the damaging consequences of UVB and UVA rays [5]. Only sunscreen products with UVB and UVA filters have been produced in recent decades. As physical sunscreens, materials such as ZnO and TiO_2 are frequently chosen. Physical sunscreens are gaining popularity because, as insoluble particles, ZnO and TiO_2 ingredients sit on top of the skin and are not absorbed systemically. As a result, physical sunscreens are generally thought to be safer than chemical sunscreens. Chemical sunscreens that absorb just UV radiation are recommended over physical sunscreens [6]. Physical sunscreens work after exposure to ultraviolet radiation. The physics of action in these physical sunscreens show optical characteristics in physical phenomena such as reflection, scattering, and absorption [7]. In this investigation, physical sunscreens with active ingredients TiO_2 and ZnO were used.

TiO_2 can effectively block UVB. The efficiency of TiO_2 as an UVB filter is very good, and it can be done to produce physical sunscreen cream products with high SPF using just TiO_2 as the active ingredient. However, in the UVB range, TiO_2 has a smaller wavelength absorption. While ZnO is less effective in UVB protection than TiO_2, it has a broad-spectrum SPF but constant absorption only in the 360–370 nm wavelength range. Making it more suited to protection against what are known as "UVA long rays" (UVA I) than TiO_2 [8]. Furthermore, using ZnO in combination with TiO_2 can boost its UVB and UVA performance. As a result, the combined TiO_2 and ZnO material is regarded as an effective material for expanding the radiation spectrum range by blocking UV radiation from UVA to UVB, this material is called broad spectrum [9].

In vivo experiments suggest that TiO_2 and ZnO materials alone cannot generate sunscreen creams with high reflectance and SPF (Sun Protector Factor) [10]. Because TiO_2 is only effective for UVB protection. While ZnO protects against UVA and UVB light, it is actually most effective in the UVA range [10]. Therefore, sunscreens must be used to shield the skin from UVA and UVB radiation and to prevent the serious illnesses that can result from exposure to these rays. Sunscreens should contain both ZnO and TiO_2 as active ingredients.

TiO_2 and ZnO ingredients in physical sunscreen have advantages such as being photostable (stable to light) and recovering from a lower potential for allergies or irritation, which makes it safe for children to be applied and especially helpful for people with acne-prone skin [11]. Physical sunscreen provides fast and effective protection without waiting for a long time for the sunscreen to penetrate the skin [12]. In addition, the active ingredient TiO_2 has disadvantages, such as a white cast on the skin's outer layer. The high refractive index of TiO_2 and ZnO can produce a very white skin appearance (white cast) due to the reflection of light mechanism [13]. Therefore, a combination collaboration is required to compensate for the weaknesses of TiO_2 by combining ZnO. ZnO has a refractive index that is smaller in the range of 1.9–2.0, giving a greater degree of transparency than TiO_2, with a range of 2.5–2.7. On the basis of past research, the Food and Drug Administration believes that a white cast on the skin can be fixed by changing the optimum composition with a concentration limit of ZnO and TiO_2 below 25%. The Food and Drug Administration (FDA) must adhere to the maximum concentration of ZnO and TiO_2 compositions in special physical sunscreen products [14]. This restriction is based on the risk of employing high quantities of ZnO and TiO_2, which can cause physical sunscreen creams to have a white cast if applied to the skin [15]. So, based on this description, it must be done to determine the effect of the composition of ZnO and TiO_2 on the white cast that will be applied to sunscreen.

However, in this study, we are interested in highlighting the effect of the composition of ZnO and TiO_2 that works on the UVA-UVB wavelength range in blocking ultra violet on effective skin and seeing the performance of the optical properties (reflectance, absorbance, transmittance, and bandgap) of these two materials in protecting the skin along the UVA-UVB wave. The optical properties of a physical sunscreen cream were analyzed using the Kubelka-Munk theory [16]. This investigation uses laboratory experiments as input data and adjusts them to the Kubelka-Munk theory, giving an indication of the sunscreen's absorption and scattering coefficients. Investigators are interested in observing the effect of the optimal composition of ZnO/TiO_2 composites on physical sunscreen products, subsequently producing physical sunscreen cream with a concentration limit of less than 25%, analyzing the optical properties using the Kubelka-Munk theory, and determining the effectiveness of these materials in UVA and UVB ranges. This is an innovative strategy for researchers to overcome the problems in previous studies so that research is being conducted on the effect of optical analysis of ZnO/TiO2 composite composition on sunscreen products using Uv-Vis spectrophotometry.

II. METHOD

This project consists of laboratory tests. The experiment took place in three locations: Material Physics and Biophysics Laboratory of FMIPA, Padang State University, for preparing ZnO and TiO_2 samples; the Chemistry Laboratory of FMIPA, Padang State University, for evaluating the characterization of samples using XRF and UV-vis spectrophotometry; and the Institute of Higher Education Services Region X (LLDIKTI) to produce physical sunscreen cream.

ZnO, TiO_2, stearic acid, cetyl alcohol, nipagin, nipasol, TEA, glycerin, VCO, and Aquadest have been used in this experiment. CV. CHEMICAL JAYA LABORA (Tokopedia) supplied the material. 50 mL of pyrex glass, stirring rods, a watch glass, a hand mixer, brushes, spatulas, drop pipettes, a hotplate, and analytical scales were utilized in this study.

The DRS UV-Vis Spectrophotometer and XRF were both used for characterization testing in the present investigation. Diffuse reflectance spectrophotometry test equipment gives information or parameters that will be inspected on physical sunscreen, such as absorption, reflectance, transmittance, and bandgap, where the four parameters are part of optical characteristics. The UV-Vis Spectrophotometer test equipment is of the UV-VIS 100 DA-X variety. The elemental composition of a material or sample is provided by XRF test equipment, and the sample analyzed is powder. Both of these instruments can be found in the Chemistry Laboratory of Padang State University's FMIPA.

The initial step is the preparation of ZnO and TiO_2 samples and characterization testing using XRF equipment, and the subsequent step is the creation of sunscreen cream base samples based on variations in the composition of ZnO and TiO_2 against physical sunscreen. The next step uses DRS UV-Vis spectrophotometry equipment to assess the physical characterization of physical sunscreen cream products, and the final step is the data analysis process.

The initial procedure is to prepare ZnO and TiO_2 samples. The TiO_2 and ZnO samples acquired at this commercial outlet are of cosmetic grade and have been extensively sold on the marketplace as cosmetic raw materials with mikrometer-sized ZnO and Nanometer-sized TiO_2. Therefore, the first phase of the experiment is to perform filtration ZnO powder using a 60-mesh sieve, which is done to make sure that the size of ZnO powder is evenly distributed and smooth. The filtered ZnO and TiO_2 powder is subsequently evaluated for XRF tool characterization, which is done to identify the content and composition of ZnO and TiO_2 powder. The following phase is to create a physical sunscreen cream sample after evaluating the purity of the material.

Sunscreen cream samples are created in two phases: the oil phase and the liquid phase. The liquid phase consists of a substance or content that is dissolved in basa water, such as TEA, glycerin, nipagin, and nipasol. While the oil phase contains ingredients that can be dissolved in acids such as stearic acid and cetyl alcohol, and VCO. These processes will result in a creamy combination. Table 3 shows the ingredients formulation that were measured before producing the physical sunscreen cream.

Table 3. The Ingredient formulation of Physical Sunscreen

Ingredient	Uses	Quantity of ingredients used (w/w)%		
		Formulation 1	**Formulation 2**	**Formulation 3**
ZnO	Physical Absorber	7,5%	2,5%	2,5%
TiO_2	Physical Absorber	5%	2,5%	2,5%
Stearic acid	Emulsifying Agent	10%	10%	10%
Stearil Alkohol	Stiffening Agent	2%	2%	2%
VCO	Antioxidants	8%	8%	-
Glycerin	Humectant	5%	5%	5%
TEA	Emulsfying Agent	2%	2%	2%
Nipagin (methyl paraben)	Anti Fungal	0,1%	0,1%	0,1%
Nipasol (propyl paraben)	Anti Bacterial	0,18%	0,18%	0,18%
Aquadest	Waterphase	Ad 100%	Ad 100%	Ad 100%

In accordance with table 3, this formula's water phase comprised triethanolamine (TEA) and aquadest. When stearic acid and TEA are combined at a temperature above the melting point of stearic acid, the process of neutralizing TEA stearate occurs. The resulting product is TEA stearate salt, also known as TEA soap. Glycerin can be used as a humectant, which acts to keep the skin moisturized. The formulation contained methyl paraben and propyl paraben preservatives. Because methyl paraben has higher activity in the fungal category and propyl paraben has more activity in the bacterial category, combining the two gives strong protection against both categories of microbes. Microbial contamination in pharmaceutical products can reduce cream preparation quality by causing discoloration, smell changes, and pH changes. Considering table 3 previous research was used to formulate this sunscreen composition, and the cream's results were obtained from the most stable formulation based on viscosity, spreadability, homogeneity, cream type, pH, organoleptic, and stability parameters [17], so this is a guideline for making sunscreen cream in this study. The phases of creating physical sunscreen cream are also depicted in figure 1 below.

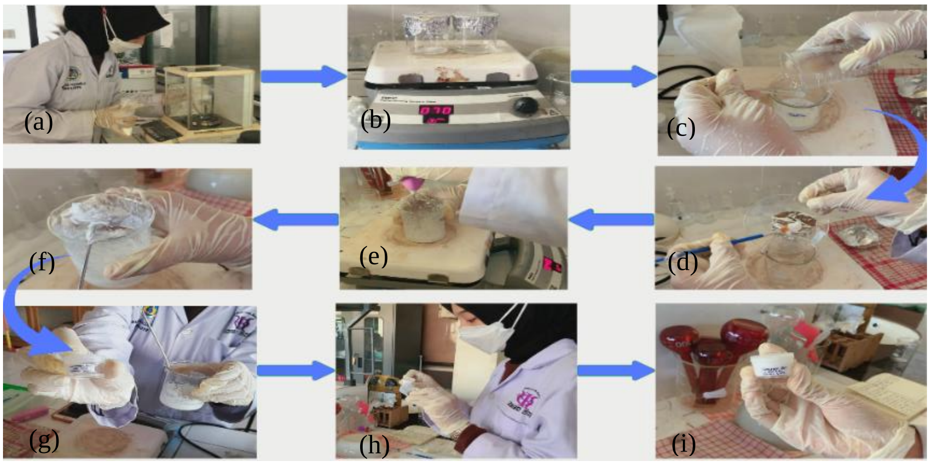


Fig. 1. Phase of creating physical sunscreen cream (a) measuring all of the ingredients (b) heated liquid phase and oil (c) add liquid phase to oil phase (d) add active ingredients (e) mixer until 5 minutes (f) cream physical sunscreen (g) putting the physical sunscreen cream in packaging (h) spread the krim on the packaging (i) cream physical sunscreen ready to use

Show figure 1, the subsequent step is the creation of a physical sunscreen cream. After measuring all of the ingredients, the oil and liquid phases are placed in two 100 ml beakers, wrapped with aluminum foil, and heated for 10 minutes on a hotplate set to 70°C. Then, similar to the composition variations given in Table 3, add the active ingredients ZnO and TiO_2, and once the materials are fully dissolved and combined, proceed gently from the liquid phase to the oil phase. The two phases are then mixed for 5 minutes with a mixer before lowering the hotplate temperature to 40°C. Mix it until a thick cream mass is formed, and then let the cream stand until homogeneous. After putting the physical sunscreen cream in packaging, it was ready for use and evaluated for physical characterization using diffuse reflectance spectrophotometry as shown in Figure 2.

Fig. 2. Diffuse reflectance spectrophotometry

As can be seen in Figure 2, The double-beam spectrophotometer with five variable slits and an advanced measurement wavelength range from 185 nm to 1200 nm, optimal for the measurement of solutions and solids such as physcial sunscreen creams with the highest demands on optical resolution, is also available as a dissolution model. The characterization findings are produced in the form of a wavelength spectrum against the reflectance R (%). The band gap energy is acquired by translating the amount of R (%) into the Kubelka-Munk factor F(R), which is a diffusion-spectrometer instrumentation, using a simple method based on Kubelka-Munk theory [18]

The third step involves utilizing a diffuse reflectance spectrophotometry to test the physical characteristics of physical sunscreen cream. Physical sunscreen was chosen for the purpose of this research because its method of action if exposed to UV radiation produces physical phenomena such as reflection, scattering, and absorption. These three phenomena are intimately related to optical characteristics investigated in Material Physics. The optical characteristics are tested using a Diffuse reflectance Spectrophotometer test instrument. There can be four parameters that will be tested: absorbance, reflectance, transmittance, and bandgap. For absorbance testing, absorbance is measured not only in the UV region but also in the visible light region. As a result, absorbance is measured at wavelengths ranging from 200 nm to 800 nm. This test was carried out by applying 0.1 grams of cream solid to a round cuvette with a brush or finger gloves. To determine the diffuse reflectance settings of the three samples, spectrophotometry must be utilized. The light source configuration and sample positioning vary between reflectance and absorbance measurements. The reflectance of the three samples was also tested with a particular sapphire container. A slide made of glass was utilized to homogenize the sample surface after a comparable quantity of each sample was placed in the sample holder. The reflectance measurements of the TiO_2 and ZnO compositions were compared to MgO optical standards in the range of visible light (400–700 nm). And is evaluated by placing the cream sunscreen into a container and then into a diffuse reflectance spectrophotometry. The data of this diffuse reflectance spectrophotometry tool measurement are percentage as reflectance (R %), transmittance (T %), and absorbance. Which is inserted into the equation [19] :

$$A + R + T = 1 \tag{1}$$

A : Absorbance
R : Reflectance (%)
T : Transmittance (%)

The final step is to process the analysis data from the Diffuse Reflectance spectrophotometer characterization. It is important to know that the formula for the physical characterization of this tool is absorbance, reflectance, transmittance, and energy (bandgap) for this data processing. Band gap energy calculation using UV-Vis Diffuse Reflectance The UV-Vis Diffuse Reflectance spectrophotometric approach is used to generate spectroscopy [20]. The calculated reflectance is the value given in the equation (2), and it is used to calculate the Kubelka-Munk equation (equation 3). The equation (3) is related to the equation (4) parameters k (absorbance coefficient) and s (diffuse reflectance scattering coefficient). As a result, the equation (5) is obtained [18]

$$R'\infty = \frac{R_\infty(sample)}{R_\infty(standart)} \tag{2}$$

$$F(R'\infty) = \frac{(1-R'\infty)^2}{2R'\infty} \tag{3}$$

$$F(R'\infty) = \frac{k}{s} \tag{4}$$

$$\frac{k}{s} = \frac{(1-R'\infty)^2}{2R'\infty} \tag{5}$$

$R'\infty$: Calculated reflectance
$F(R'\infty)$: Kubelka-Munk
k : Absorbance coefficient
s : Diffuse reflectance scattering coefficient

III. RESULTS AND DISCUSSION

The current research successfully produced physical sunscreen products in the form of creams with three composition ratios of ZnO/TiO_2, especially ZnO/TiO_2 10% (7.5%; 2.5%), $ZnO-TiO_2$ 5% (2.5%; 2.5%), and ZnO/TiO_2 5% (2.5%; 2.5%), without being treated with VCO. Several characterization test tools can be used to examine the effect of adding ZnO/TiO_2 to physical sunscreen. The XRF test can determine the content and composition of the ZnO and TiO_2 powders. For the results of XRF testing of ZnO purity, more details can be seen in Table 1.

Table 1. XRF Testing of ZnO Purity

Element		Geology		Oxide	
Component	**Conc**	**Component**	**Conc**	**Component**	**Conc**
Al	0,296 %	Al_2O_3	0,5 %	Al_2O_3	0,453 %
Si	0,256 %	SiO_2	0,492 %	SiO_2	0,442 %
P	0,724 %	P_2O_5	1,445 %	P_2O_5	1,335 %
Cl	0,092 %	Cl	0,081 %	CaO	39,644 %
Ca	36,325 %	CaO	44,292%	TiO_2	0,008%
Ti	0,006 %	Ti	0,005 %	V_2O_5	0,002%
V	0,001 %	V	0,001 %	Fe_2O_3	0,062 %
Fe	0,057 %	Fe_2O_3	0,07 %	Co_3O_4	0,004%
Co	0,004 %	Co	0,004 %	NiO	0 %
Ni	0 %	Ni	0 %	ZnO	57,37 %
Zn	61,525 %	Zn	52,486%	SrO	0,023%
Sr	0,027 %	Sr	0,023 %	Ag_2O	0,526 %
Ag	0,619 %	Ag	0,543 %	CdO	0 %
Cd	0 %	Cd	0 %	Yb_2O_3	0,058%
Yb	0,067 %	Yb	0,058 %	Cl	0,073 %

In the table 1, the purity results of ZnO powder are shown. The results show that the components included in ZnO powder are Al, Si, P, Cl, Ca, Ti, V, Fe, Co, Ni, Zn, Sr, Ag, and Yb. The purity contained in ZnO powder is just 57.37%, and another high percentage component is CaO with a content of 39.64%. So that the quality of ZnO powder is not 100% pure. And to test the purity of TiO_2, see Table 2.

Table 2. XRF Testing of TiO_2 Purity

Element		Geology		Oxide	
Component	**Conc**	**Component**	**Conc**	**Component**	**Conc**
Al	0,322 %	Al_2O_3	0,604 %	Al_2O_3	0,472 %
Si	0,296 %	SiO_2	0,629 %	SiO_2	0,49 %
P	0,53 %	P_2O_5	1,206 %	P_2O_5	0,936 %
Ca	0,268 %	CaO	0,371 %	CaO	0,258 %
Ti	97,383 %	Ti	95,99 %	TiO_2	96,985 %
Cr	0.002 %	Cr	0,002 %	Cr_2O_3	0,001%
Fe	0,031 %	Fe_2O_3	0,044 %	Fe_2O_3	0,024 %
Ge	0 %	Ge	0 %	GeO_2	0%
Ag	0,807 %	Ag	0,804 %	Ag_2O	0,607 %
Cd	0 %	Cd	0 %	CdO	0 %
I	0,332 %	I	0,328%	Tm_2O_3	0,002 %
Tm	0,005%	Tm	0,002 %	Lu_2O_3	0,014 %
Lu	0,023%	Lu	0,02 %	PtO_2	0 %
Pt	0,001%	Pt	0,001 %	I	0,21%

The purity findings of TiO_2 powder are shown in Table 2. The components found in TiO_2 powder are Al, Si, P, Ca, Ti, Cr, Fe, Ge, Ag, Cd, I, Tm, Lu, and Pt, and the purity of TiO_2 powder is 96.98%. As a result, the purity of TiO_2 powder is nearly 100%. This study TiO_2 and ZnO were used for the production of physical sunscreen with a purity of 96.98% and 57.37%.

The next characterization test tool is a UV-Vis spectrophotometer. The UV-Vis Spectrophotometer test instrument can determine absorbance, transmittance, reflectance, and energy gap values. The findings of characterization using an UV-Vis spectrophotometer for ZnO/TiO_2 physical sunscreen seeks to identify the values of absorbance, reflectance, transmittance, and energy gap. For sample testing, the tool utilized is an UV-Vis Spectrophotometer with the UV VIS 100 DA-X type and diffuse reflectance spectrophotometry , with the lowest allowable wavelength of 185–210 nm and the highest at 800-1100 nm. Sample testing had been carried out in the Chemistry Laboratory of the Faculty of Mathematics and Natural Sciences at Padang State University. The following are the findings of UV-Vis spectrophotometer evaluation of ZnO/TiO_2 physical sunscreen with three variations of 10%, 5%, and 5% without VCO for absorbance, transmittance, and reflectance values, as shown in Figure 3.

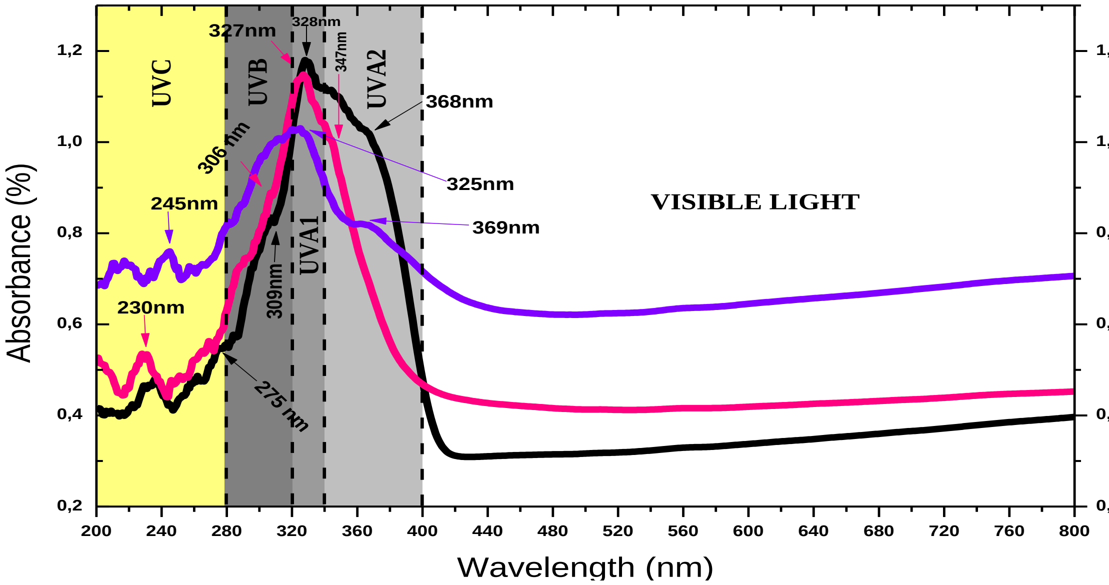
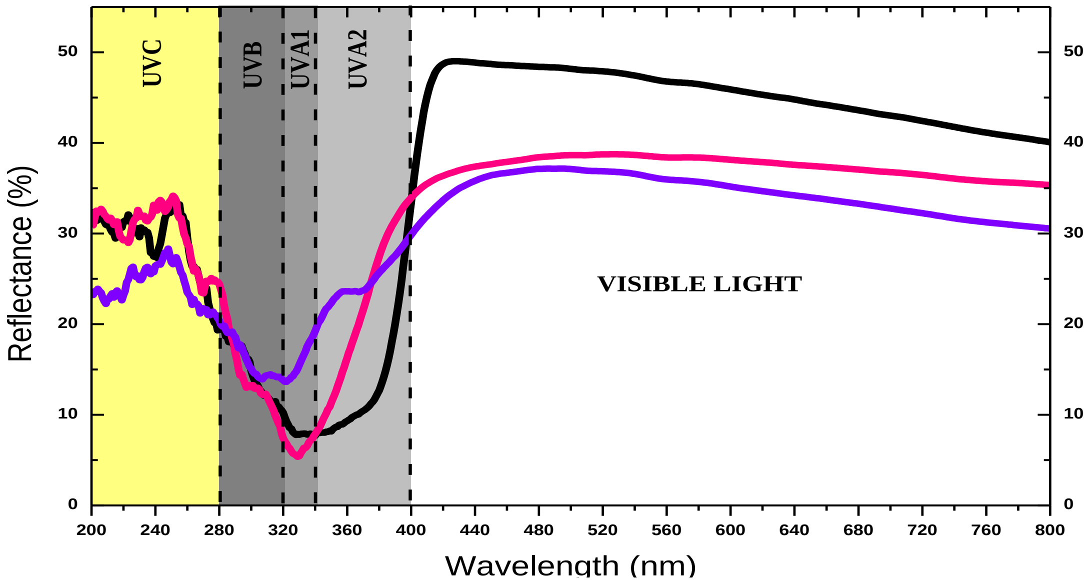
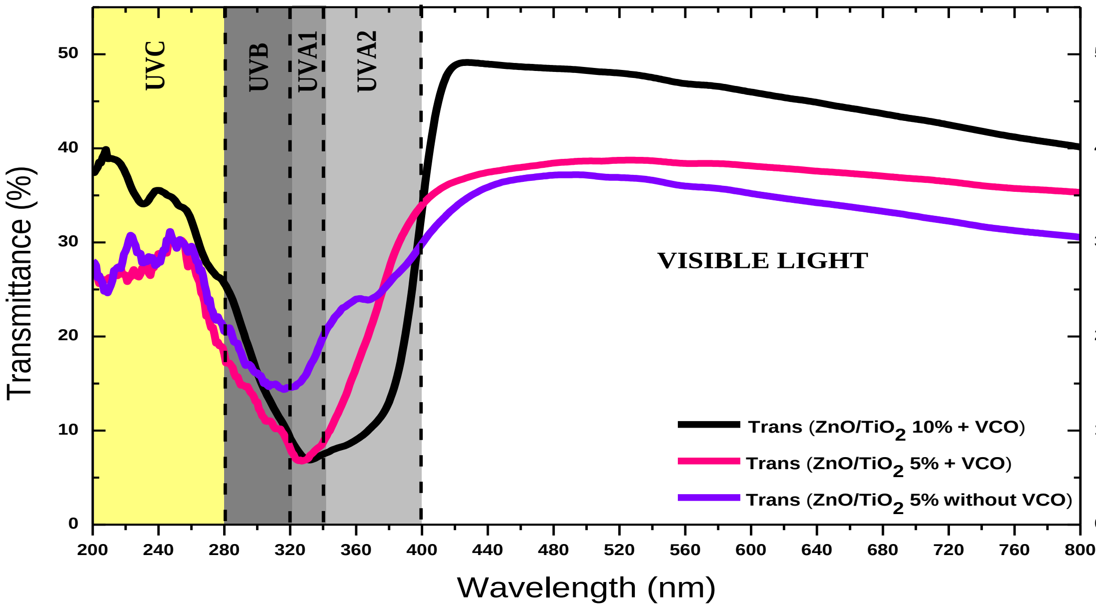


Fig. 3. Absorbance (a) 10% + VCO (b) 5% + VCO (c) 5% without VCO

Figure 3 shows that three samples had the highest absorbance maximum in the UV spectrum. Furthermore, the percentage of ZnO/TiO_2 in the cream ingredients (% w/w) determines the height of this absorbance maximum. Because the concentration of ZnO/TiO_2 in the cream composition increases, this affects the sample's absorbance maximum. The results showed that samples with ZnO/TiO_2 10% + VCO concentration had a reasonably high absorption wave in UVA1, with a wavelength of 328 nm and an absorbance peak of 0.993 au. In terms of ZnO/TiO_2 concentration variation, 5% + VCO has wave absorption in UVA 1 with a wavelength of 327nm and an absorbance peak of 0.961 au. And while the change in ZnO/TiO_2 concentration without VCO has a low absorption, it is still 0.842 au in UVA1 with a wavelength of 325 nm. Furthermore, 10% and 5% sample variations with the addition of VCO are more effective because the UV protection in the UVA-UVB curve is higher, but the variation without the addition of VCO has low UVA-UVB absorption. On the other hand, the provision of antioxidants such as Virgin Coconut Oil (VCO) is a simple way to neutralize Reactive Oxygen Species (ROS) radical chemicals contained in the combination of sunscreen creams. besides that the content of VCO can reduce the whiteness of the skin [17]. Antioxidants can reduce the amount of white cast and ROS produced during UV irradiation [21]. As a result, the addition of VCO affects the formulation of the physical sunscreen cream. Figure 4 depicts the reflectance.



(a) Reflectance

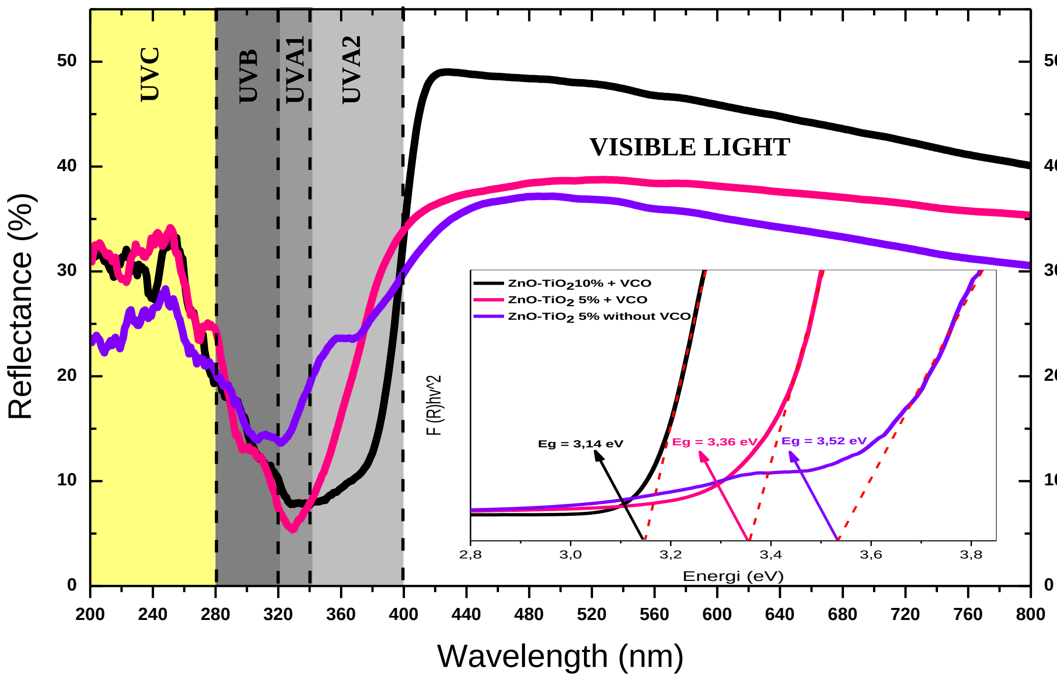


(b) Transmittance

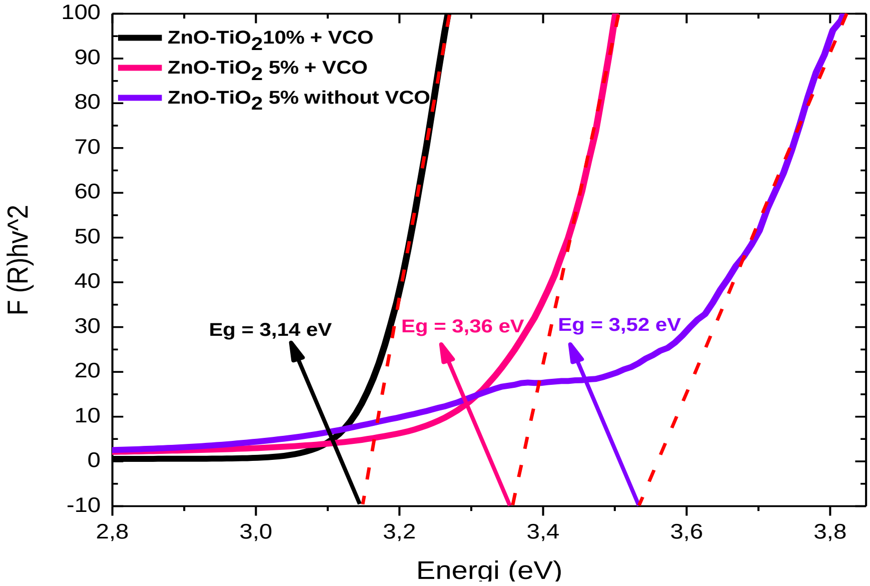
Fig. 4. (a) Reflectance (b) Transmittance

According to Figure 4, the acquired findings are the reflectance of the three sample variants. The higher the percentage of reflectance or scattering in a radiation area, the lower the transparency. Physical sunscreen is known to provide more effective protection when the reflection is high. The reflectance percentage of the three samples is fairly low in the UV and visible light regions (30%–40%), but it will increase in the infrared zone. The samples' enhanced reflection in the infrared range implies that ZnO/TiO_2 has low transparency in that region. Furthermore, Figure 4 demonstrates that all three materials exhibit very poor transparency in the visible light violet (400–450 nm) and red (620–750 nm) ranges.

The energy gap values obtained using the Kubelka-munk method for the ZnO/TiO_2 Physical sunscreen UV-Vis spectrophotometer characterization with three composition variations, namely 10%, 5%, and 5% without VCO, are shown in Figure 5.



(a) Reflectance Kubelka-Munk



(b) bandgap (eV)

Fig. 5. (a) Reflectance Kubelka-Munk (b) Bandgap

Figure 5 shows that the energy gap values of ZnO/TiO_2 for changes of 10%, 5%, and 5% without VCO are 3.14, 3.36, and 3.52 eV, respectively. According to the results, the higher the ZnO/TiO_2 composition, the lower the energy gap value. The smaller the energy band gap (between the conduction band and the valence band), the easier it is for electrons on the valentine band to jump into the conductive band [22]. The smaller the energy band gap (between the conduction band and the valence band), the easier it is for electrons on the valentine band to jump into the conductive band [20]. Given that the overlapping tape is caused by recombination of electrons and holes across the conduction and valence tapes (band gap) and the emission of shallow surface traps due to oxygen vacuum trap (Vo) conditions, it was concluded that the energy of the gap generated for each change was within the energy gap range of semiconductor materials. The semiconductor (ZnO/TiO_2) gap energy range is set at 3,1-3,5 eV [23].

IV. CONCLUSION

Based on studies done on the effects of variations in the ZnO/TiO_2 composition on optical properties such as absorption, reflection, transmission, and the physical bandgap of sunscreen using the Kubelka Munk theory, it can be indicated that the composition of the ZnO/TiO_2 composite affects the optical analysis of the physical sunscreen in visible light and ultra violet light. UV-vis spectroscopy characterization showed that the ZnO/TiO_2 composite absorbed more effectively in the ultra violet range than in visible light, and the greatest absorption and maximum reflectance are in the UVA1 range. The cream formula's maximal absorptive height increases with increasing ZnO concentration (% w/w). The higher the UV light reflection, the lesser the transparency of visible light. The bigger the $ZnO-TiO_2$ concentration, the greater the band gap value of the physical sunscreen, which is in the range of 3.1–3.5 eV. Based on this finding, ultraviolet (UV) protection using ZnO/TiO_2 as an active component and the addition of VCO have the potential to be developed and tested further in the future.

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REFERENCES

[1] J. D. Orazio, S. Jarrett, A. Amaro-ortiz, and T. Scott, "UV Radiation and the Skin," *Int. J. Mol. Sci*, vol. 14, pp. 12222–12248, 2013, doi: 10.3390/ijms140612222.

[2] J. Krutmann, "Ultraviolet A radiation-induced biological effects in human skin: Relevance for photoaging and photodermatosis," *J. Dermatol. Sci.*, vol. 23, no. SUPPL. 1, pp. 22–26, 2000, doi: 10.1016/S0923-1811(99)00077-8.

[3] E. Dupont, J. Gomez, and D. Bilodeau, "Beyond UV radiation: A skin under challenge," *Int. J. Cosmet. Sci.*, vol. 35, no. 3, pp. 224–232, 2013, doi: 10.1111/ics.12036.

[4] R. Jonuarti, F. Haryanto, and Suprijadi, "Preliminary investigation of boron nitride nanotubes as an active material of sunblock," *J. Phys. Conf. Ser.*, vol. 1876, no. 1, 2021, doi: 10.1088/1742-6596/1876/1/012007.

[5] S. Pavel, "Light therapy (with UVA-1) for SLE patients: Is it a good or bad idea?," *Rheumatology*, vol. 45, no. 6, pp. 653–655, 2006, doi: 10.1093/rheumatology/kel063.

[6] G. P. Dransfield, "Inorganic sunscreens," *Radiat. Prot. Dosimetry*, vol. 91, no. 1–3, pp. 271–273, 2000, doi: 10.1093/oxfordjournals.rpd.a033216.

[7] O. P. Egambaram, S. Kesavan Pillai, and S. S. Ray, "Materials Science Challenges in Skin UV Protection: A Review," *Photochemistry and Photobiology*, vol. 96, no. 4. Blackwell Publishing Inc., pp. 779–797, Jul. 01, 2020. doi: 10.1111/php.13208.

[8] M. Battistin *et al.*, "A new approach to UV protection by direct surface functionalization of TiO2 with the antioxidant polyphenol dihydroxyphenyl benzimidazole carboxylic acid," *Nanomaterials*, vol. 10, no. 2, pp. 1–19, 2020, doi: 10.3390/nano10020231.

[9] B. L. Diffey, P. R. Tanner, P. J. Matts, and J. F. Nash, "In vitro assessment of the broad-spectrum ultraviolet protection of sunscreen products," *J. Am. Acad. Dermatol.*, vol. 43, no. 6, pp. 1024–1035, 2000, doi: 10.1067/mjd.2000.109291.

[10] H. W. L. Samantha L. Schneider, "A Review Of Inorganic UV Filters Zinc Oxide and Titanium Dioxide." Photodermatol Photoimmunol Photomed, pp. 442–446, 2019.

[11] H. Pratt *et al.*, "UV imaging reveals facial areas that are prone to skin cancer are disproportionately missed during sunscreen application," *PLoS One*, vol. 12, no. 10, pp. 1–14, 2017, doi: 10.1371/journal.pone.0185297.

[12] W. Lyu, M. Qian, and F. Yang, "Nanoparticles in sunscreen: exploration of the effect and harm of titanium oxide and zinc oxide," *Highlights Sci. Eng. Technol.*, vol. 13, pp. 155–162, 2022, doi: 10.54097/hset.v13i.1345.

[13] R. Jonuarti, T. D. . Wungu, and F. Haryanto, "Gel tabir surya berbahan aktif titanium dioksida dengan beberapa variasi perbandingan konsentrasi dalam carbopol (1% b/b).," *Pros. Semin. Nas. Fis.*, vol. 5.0, pp. 391–396, 2019.

[14] Food and Drug Administration (US), "Sunscreen Drug Products for Over-the-Counter Human Use," *Federal Register*, 2019. https://www.federalregister.gov/documents/2019/02/26/2019-03019/sunscreen-drug-products-for-over-the-counter-human-use (accessed Jun. 23, 2023).

[15] G. Tortini *et al.*, "Criticisms in the Development of High-Protection and Broad-Spectrum 'Natural/Organic' Certifiable Sunscreen," *Cosmetics*, vol. 9, no. 3, pp. 1–18, 2022, doi: 10.3390/cosmetics9030056.

[16] M. H. Brill and M. Vik, "Encyclopedia of Color Science and Technology," *Encycl. Color Sci. Technol.*, no. January, 2020, doi: 10.1007/978-3-642-27851-8.

[17] B. C. Jayati, R. Annisa, A. F. Firdausy, and ..., "Effect of Addition Virgin Coconut Oil (VCO) on Physical Stability and SPF Value of Sunscreen Cream Combination of Zinc Oxide and Titanium Dioxide," *Proc. ...*, pp. 8–14, 2021, [Online]. Available: http://conferences.uin-malang.ac.id/index.php/planar/article/view/1453

[18] M. M. Khan, S. A. Ansari, M. I. Amal, J. Lee, and M. H. Cho, "Highly visible light active Ag@TiO2 nanocomposites synthesized using an electrochemically active biofilm: A novel biogenic approach," *Nanoscale*, vol. 5, no. 10, pp. 4427–4435, 2013, doi: 10.1039/c3nr00613a.

[19] M. Volterrani, A. Minelli, M. Gaetani, N. Grossi, S. Magni, and L. Caturegli, "Reflectance , absorbance and transmittance spectra of bermudagrass and manilagrass turfgrass canopies," pp. 1–13, 2017.

[20] Jumardin, A. Maddu, K. Santoso, and Isnaeni, "Karakteristik Sifat Optik Nanopartikel Karbon (Carbon Dots) Dengan Metode Uv-Vis Drs (Ultraviolet-Visible Diffuse Reflectance Spectroscopy)," *JFT J. Fis. dan Ter.*, vol. 9, no. 1, pp. 1–15, 2022, doi: 10.24252/jft.v9i1.28815.

[21] D. Montesano, L. Cossignani, G. D'Arco, M. S. Simonetti, and P. Damiani, "Pure lycopene from tomato preserves extra virgin olive oil from natural oxidative events during storage," *JAOCS, J. Am. Oil Chem. Soc.*, vol. 83, no. 11, pp. 933–941, 2006, doi: 10.1007/s11746-006-5049-3.

[22] J. J. Reinosa, P. Leret, C. M. Álvarez-Docio, A. Del Campo, and J. F. Fernández, “Enhancement of UV absorption behavior in ZnO-TiO2composites,” *Bol. la Soc. Esp. Ceram. y Vidr.*, vol. 55, no. 2, pp. 55–62, 2016, doi: 10.1016/j.bsecv.2016.01.004.
[23] J. J. Reinosa, C. M. Á. Docio, V. Z. Ramírez, and J. F. F. Lozano, “Hierarchical nano ZnO-micro TiO2 composites: High UV protection yield lowering photodegradation in sunscreens,” *Ceram. Int.*, vol. 44, no. 3, pp. 2827–2834, 2018, doi: 10.1016/j.ceramint.2017.11.028.