Study of the Titanium Dioxide Nanoparticles Used as UV absorber on Natural Herbal Extract Sunscreen Products

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Abstract. This research focuses on the effects of UV absorber on natural herbal extracts including Wan Nga-chang (Ivory) and Wan Tan-diao containing Glycoside and Tannin with solvent prepared via the maceration method. The concentrations of UV absorber in this study, Titanium Dioxide (TiO_2), were varied from 5, 10, 15 % by weight and compared to the unadded reference material. The characteristics and properties of sunscreen products were analyzed by UV-Vis spectroscopy, X-ray diffraction technique (XRD) and Fourier Transform-Infrared spectrometer (FT-IR). The results of the experiment showed that the optimal concentration of UV absorber is herbal cream and TiO_2 at concentrations of 10%wt. From XRD and FT-IR techniques confirmed the elements and functional group of herbal extract and TiO_2, respectively.

Keyword. Titanium Dioxide Nanoparticles, UV-absorber, Natural Herbal Extract, Sunscreen Products

1 Introduction

At present, the greenhouse effect results in global warming, the penetration of sunlight, especially UV rays can enter Earth's atmosphere increase, therefore overexposure to UV rays will result in premature skin aging, wrinkles, uneven skin tone, dullness, freckles, skin cancer and destroy the genetic system [1-3]. Due to such problems from the melanin process under the skin through the enzyme Tyrosinase. To reduce those problems can be done by inhibiting the Tyrosinase enzyme [4-5] by natural extracts in the group of Glycoside and Tannin. It can inhibit the Tyrosinase enzyme. In addition, glycosides and tannins are also antioxidants and can be anti-inflammatory and antibacterial activity [6-8]. There are many methods of extracting natural substances from herbs, such as maceration, ultrasonic extraction, microwave extraction, and continuous extraction [6,8]. This research is focused on natural herbal extracts obtained from Wan Nga-chang (Ivory) and Wan Tan-diao in the group of glycosides and tannins, respectively. Using the natural extract is the method aiming to the sustainable production and fit to the bioeconomy and green economy. Glycoside is a molecule in which a sugar is bound to another functional group via a glycosidic bond. Glycosides play numerous important roles in living organisms [9]. Tannin is a class of astringent, polyphenolic biomolecules that bind to and precipitate proteins and various other organic compounds including amino acids and alkaloids [9]. Wan Nga-chang or Ivory, the scientific name: *Sansevieria stuckyi* is a plant in the family Agavaceae. It is an herbaceous plant. There are underground stems, no leaves, and green stems emerging from the soil. Shaped like ivory. The inflorescences or florets are white and fragrant [9] as shown in Figure 1. Wan Tan-diao, the scientific name: *Hypoxis aurea* Lour, is a plant in the family Hypoxidaceae. It is a tuberous herb with underground stems and round roots. The leaves are slender, elongated like blades of grass in a straight line, about 10-30 cm long, about 2-3 mm in width, and the flowers are single or paired with golden yellow flowers. For flower stalks about 2.5-10 cm long [9] as shown in Figure 2. This research is focusing the maceration method. Maceration is the process of fermentation of herbs with solvent until the tissue of the herb is soft and the solvent penetrates and dissolves the herb to produce an extract. It is also the most popular method by which the solvent suitable for the herb can be selected. The advantage of this method is that the extract is not heated and can reduce the chance of decomposition of the extract. Whereas, it will be wasted because many solvents are required [6]. Using herbal extracts to make cosmetic products, such as sunscreen is an interesting alternative for people allergic to chemical makeup.

This research focused on the assessment of the influence of Titanium dioxide nanoparticles (TiO_2) as a UV absorber material on sunscreen products from natural herbal extracts including Wan Nga-chang (Ivory) and Wan Tan-diao. These compounds are classified in the group of glycoside and tannin with solvent through the maceration method. After that, the influence of nano-titanium dioxide concentration on the light absorption of sunscreen products from natural herbal extracts was

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studied. The characteristics and properties of sunscreen products with optical techniques by UV-Vis spectroscopy, elements in herbal extracts by X-ray diffraction technique (XRD) and functional group by FT-IR were analyzed.

Figure 1. The appearance of Wan Nga-chang (Ivory)

Figure 2. The appearance of Wan Tan-diao

2 Materials and methods

2.1 Extraction method of Ivory and Wan Tan Diao

Herb extract was comprised of Ivory and Wan Tan Diao by the solvent extraction or maceration technique. Maceration used the solvent that was cold pressed coconut oil in a solvent to herbal ratio of 2:1 as shown in Figure 3. The extracts from Wan Nga-chang (Ivory) and Wan Tan-diao were mixed with a ratio of 1:1 and solvent and the samples were stirred for 30 minutes.

2.2 Herbal cream preparation

The herbal cream preparations have three main components: water base, oil base and co-solvent. The mixed extracts from section 2.1 used oil base, whereas TiO_2 at the concentrations of 0, 5, 10 and 15 %w/w used RO water base. For co-solvent, viscolam AT 100P was used. The ratio of the three main components between water base, oil base and co-solvent are 75:23:2. These components were mixed with a homogenizer for 30 minutes, then rested for 10 minutes. This step was repeated for 3 times, and leaved it for 1 night for setting the cream as shown in Figure 4.

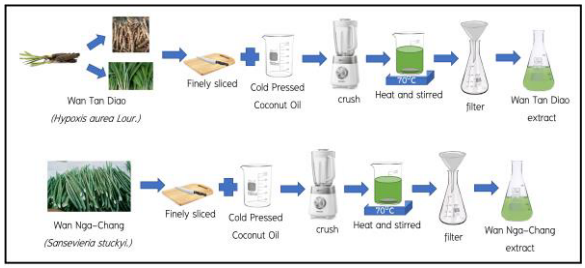

Figure 3. Herbal extraction method

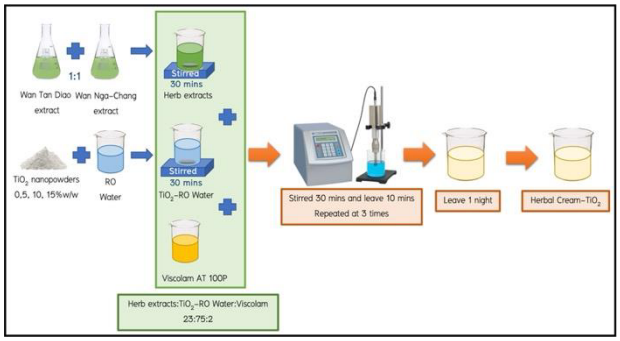

Figure 4. Herbal cream preparation

2.3 Films preparation

The glass substrates were cut in size of 2×2 cm^2, then cleaned with detergent, ultrasonicated in DI water, acetone, and isopropanol for 15 min in each step, and dried with nitrogen gas. The extracts that were mixed with TiO_2 with varying concentrations of 5, 10, 15%w/w were coated by doctor blade technique on the glass substrate compared with herbal cream, then substrate was dried for 30 min at 80 °C. The method was summarized as seen in Figure 5.

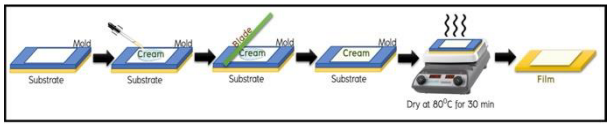

Figure 5. Films preparation

2.4 Characterization and measurements

Fourier transform infrared (FTIR) spectroscopy was used to identify the chemical structure of the films and possible interactions between their components. The FT-IR spectra of the films were measured from the wave number 500 – 4,000 cm^{-1} by Perkin Elmer UATR Two spectrophotometer. UV absorbance was characterized by UV-Vis spectroscopy PG Instrument with model T92+

Spectrophotometer in absorbance mode from the wavelength 200 - 800 nm. The crystalline properties of films were analyzed from X-ray diffraction (XRD) patterns obtained from scanning 2-theta from 10-80° at a fixed incident angle of 0.4° (Rigaku Smartlab using Cuk-alpha as the X-ray source) using X-ray diffractometer with Cu Kα radiation (λ=0.15406 nm).

3 Results and discussion

3.1 UV absorption

Figure 6 presents UV absorbance from 250 to 800 nm of herbal cream and TiO_2 at various concentrations compared with herbal cream. Especially, the UV absorption range from 300-400 nm, it was shown that the intensity of herbal cream and TiO_2 at concentrations of 5 and 10%wt increased, however, at TiO_2 15%wt, the intensity was decreased. The trend of this graph shows the optimal concentration of UV absorbers is herbal cream and TiO_2 at concentrations of 10%wt.

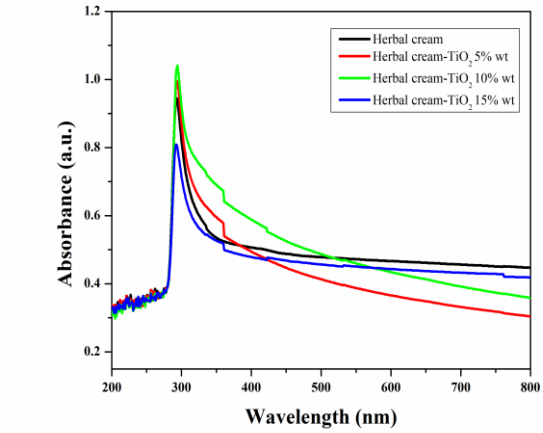

Figure 6. UV absorbance of herbal cream and TiO_2 at various concentrations

3.2 X-ray diffraction characterization

Figure 7 shows X-ray diffraction pattern of a commercial grade Titanium (IV) oxide nanoparticle (TiO_2 P25). It presents a mixed phase between anatase and rutile structure by comparing with the data for Titanium (IV) oxide (TiO_2) in anatase phase (A) from the JCPDS files no. 21-1272 and it has the highest intensity peaks at the (101) (004) (200) (105) (211) plane that corresponds to the position of the 2θ values are 25.31°, 37.80°, 48.04°, 53.89°, 55.06°, respectively. The Titanium (IV) oxide in rutile phase (R) data from the JCPDS file no. 21-1276 has the highest intensity peak at the (110) plane that corresponds to the position of the 2θ value is 27.44° [3]. Each phase is a tetragonal structure.

Figure 8 shows a typical XRD pattern of mixed herbal cream and TiO_2 at various concentrations. The herbal cream reference presents that herbal extracts did not show any pronounced structure due to the uniqueness of the organic compounds. For the mixtures where titanium dioxide was added at different concentrations, it was seen that the peak was formed due to the mixing of the rutile phase and the anatase phase of the titanium dioxide and the graph intensity was the highest at a concentration of titanium dioxide of 15% by weight.

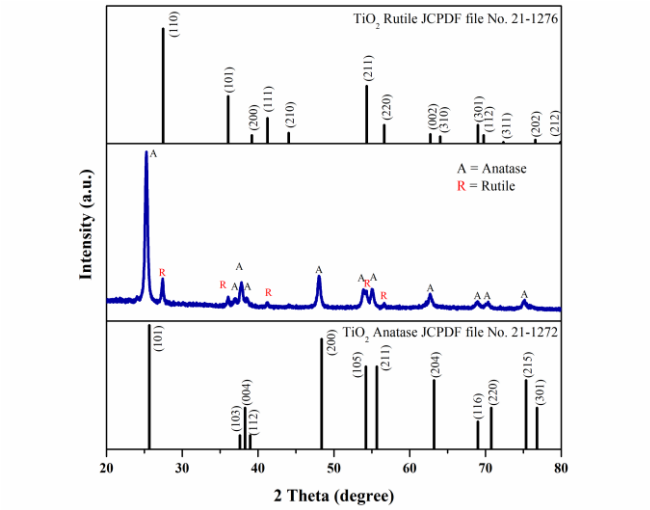

Figure 7. X-ray diffraction patterns of Titanium (IV) oxide nanoparticles commercial grade (TiO_2 P25)

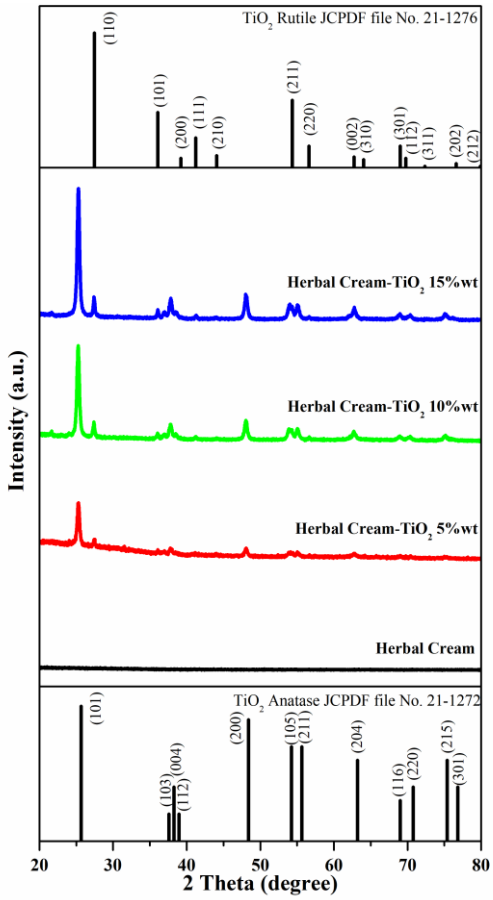

Figure 8. X-ray diffraction pattern of herbal cream and TiO_2 at various concentrations

3.3 Fourier Transform-Infrared spectrometer (FT-IR)

Figure 9 shows FT-IR curves of TiO_2 powder, herbal cream and herbal cream with TiO_2 absorbent material at

the ratios of 5%, 10%, and 15% by weight, respectively. For TiO_2 powder, the oscillations between the titanium atom and the oxygen atom inside the molecule are observed at the wave number 523 cm^{-1} representing by the titanium and oxygen oscillations as a stretching oscillation (Ti-O Stretching) [3]. FT-IR spectra of herbal cream show oscillatory characteristics of tannin and glycoside extracts. Tannin shows a wide peak in the region 3550–3100 cm^{-1} that is characteristic of the OH stretching vibration of benzene nucleus and methylol group of tannin. A small peak around 2900 cm^{-1} is aromatic CH stretching vibration of both methyl and methylene groups. The carboxyl-carbonyl group appears at 1732 cm^{-1} in the spectrum of tannin. The bands at 1324 and 1037 cm^{-1} are symmetrical and asymmetrical C–O valence vibration. The peaks around 910-740 cm^{-1} in all spectra are deformation vibrations of the C-H bond in the benzene rings [10]. Glycoside observed the hydroxyl stretching between the wavenumbers 3319 - 3379 cm^{-1}, alkane stretching was observed between 2918 - 2947 cm^{-1}, carbonyl groups between 1719 - 1728 cm^{-1}, alkene stretching between 1641 - 1662 cm^{-1}, ether groups. between 1054 - 1070 cm^{-1} and alkene bending between 870 - 895 cm^{-1}, respectively [11]. FTIR spectrum of blended sample between herbal cream and TiO_2 at different concentrations showed that the mixed peaks of tannin and glycoside from herbal cream and TiO_2. Therefore, it can be concluded that mixed TiO_2 into herbal creams is possible without interaction with each other until the structure of TiO_2 changes.

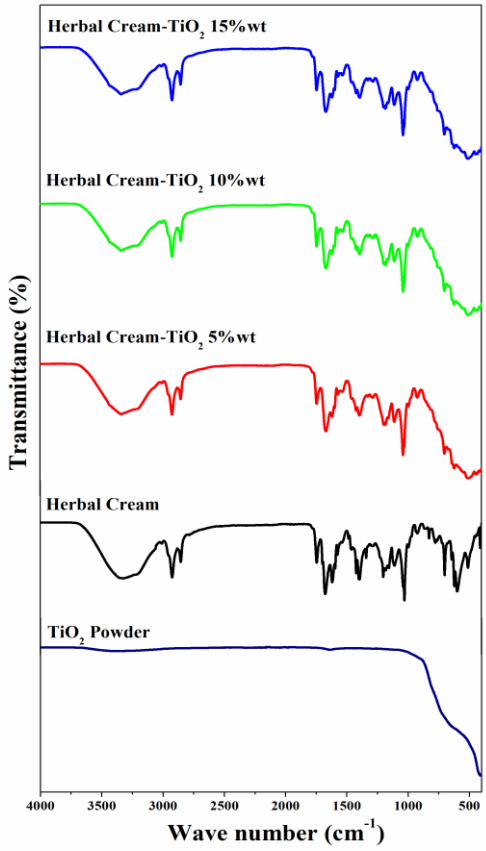

Figure 9. FTIR spectrum of herbal cream and TiO2 at various concentrations

4 Conclusion

Since most of the sunscreens in the market are chemically synthesized, it is not suitable for some people with sensitive skin. This research is therefore interested in developing a sunscreen from an easy-to-find herbal precursor. It is cheap, mass-produced in Thailand, and researched to add UV absorbers and find the right ratio between herbal extracts and UV absorbers. From this research, it was found that the optimal ratio was the UV absorbent ratio at 10% by weight, which can absorb UV rays in the range of 300-400 nm with the most effectively. This project will study more in the extracts of other medicinal plants for further comparison.

Acknowledgements

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