Ready-to-Use Titanium Dioxide Slurry for Cosmetics Application

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Abstract

The objective of research was to prepare ready-to-use TiO_2 in slurry form for easy use in cosmetics. Three types of TiO_2 source were prepared as TiO_2 slurry, namely commercial TiO_2 (TiO_2-A and TiO_2-P25) and synthesized TiO_2 (TiO_2-S) The suitable of solvents and amount of TiO_2, including optimum sonication time were studied. The experiments were set up as two groups of solvent, i.e. (1) six types of pure solvent and (2) nine types of mixed solvent. In order to achieve the best result of using solvent, 0.0075 g TiO_2 powder was added to each of 15 mL solvent and sonicated for 10 minutes. The results showed that butylene glycol (BG) was the best of pure solvent, and mixture of propylene glycol (PG) and BG ratio 1:1 was the best of mixed solvent. Due to lower cost of PG than BG, PG mixed with BG was chose as the solvent for slurry preparation. The amount of $TiO_2$was varied from 10-60% w/v of BG. Best slurry texture obtained using 60 %w/v of TiO_2. The study of sonication time was varied from 10-60 minutes. It was found that the optimum time was at 30 minutes. Texture and stability of prepared slurry were similar to commercial. Different sunscreen were formulated by containing prepared and commercial slurry separately and evaluated. There were no significant difference results between prepared slurry and commercial. In order to investigate the satisfaction of products, 40 volunteers were asked to use products for one week and answer in the questionnaires. The product containing prepared slurry was satisfied by 96% of volunteers, whereas the product containing commercial slurry was satisfied by 76% of volunteers.

Keywords : Titanium dioxide slurry, Titasol, Ready-to-Use TiO_2, Cosmetics, Sunscreen

Introduction

Nanotechnology and nanomaterials has been plays an important role in human life (Kimbrell, 2007, p. 117) making humans more comfortable living. Nowadays, there are many applications in various fields, such as medicine (Miraftab, 2017, p. 301) engineering (Profire & Constantin, 2019, p. 421) agriculture (Chaudhry, N, 2018, pp. 196-200) industry (Singh, 2017, pp. 185-191) and biotechnology (Panahi et al., 2018, pp. 15550-15558) Nanomaterials are materials that can be synthesized for obtaining particle sizes 1–100 nm. Titanium Dioxide (TiO_2) is one choice that can be synthesized and classified because of interesting properties, i.e. high refractive index, large energy band-gap, and a good property for using as photocatalyst.

TiO_2, commercial name is Titanic anhydride or Titania (Greenwood & Earnshaw, 1984, pp. 1117–19) It has three types of chemical structure namely anatase, rutile, and brookite. The difference of the three structures is caused by the distortion shape and the arrangement of each octahedral. Anatase structure is formed by arrangement with each other using the top, the rutile structure is formed by arrangement with each other using the edge, and the brookite crystal structure is formed by arrangement with each other using both the top and the edge of each octahedral. (Oi et al., 2016, pp. 108741–108754) These different arrangements of atoms in the three structures that are make different properties. The properties of brookite structures have an orbital crystal structure is orthorhombic, if it is heated more than 750 ^{o}C, will change into a tetragonal of rutile form. Anatase structure is a tetragonal structure, if moderately heated above 915 ^{o}C to change the crystal structure to rutile. Energy gap of TiO_2 is 3.20 eV (Scanlon et al., 2013, pp.798-801) When it was stimulated by higher energy than energy band gap, electrons jump up from the surface, electrons holes occurred, and will create free radicals of hydroxyl radicals, which are the gases and unstable. TiO_2 has been developed to make the particles smaller, thus having sun protection properties that can be used in sunscreen cream because this material helps to prevent radiation from the sun during 260-700 nm and can prevent visible and invisible radiation by using the principle of instantaneous radiation reflection that can prevent sunlight (Ibrahim et al., 2019, pp. 953-962) For these reasons, TiO_2 has been applied to use as an ingredient in cosmetics for sun protection. However, the limitation of using TiO_2 in powder form is non-homogeneous texture when adding in some liquid cosmetics. TiO_2 is the substance which hard to dissolve with general polar and non-polar solvent, separate from these solvent by precipitation in the short time when contact with these solvent.

Consequently, from these interesting properties of TiO_2 and the limitation for using TiO_2 powder in cosmetics, the researchers of this research realized the importance of TiO_2 in slurry form preparation for ready to use in cosmetics.

Objectives

The objectives of this work were;

1. To prepare TiO_2 slurry for using as an ingredient in cosmetics.

2. To study the suitable solvent, amount of TiO_2 and time of ultrasonic for preparing TiO_2 slurry.

3. To prepare sunscreen cream using prepared TiO_2 slurry and commercial slurry (Titasol S-35).

4. To investigate the satisfaction of volunteers after using both sunscreens creams containing prepared TiO_2 slurry and commercial slurry.

Research methodology

1. Synthesis and characterization of TiO_2

TiO_2 was synthesized followed by previous report (Pijarn, Jeimsirilers & Jinawath, 2013, pp. 661-666) and used as TiO_2 slurry in comparison to commercial (TiO_2-A and TiO_2-P25). TiO_2 was characterized with various techniques as following; Morphology of TiO_2-S, TiO_2-A, and TiO_2-P25 were observed by Scanning Electron Microscope (SEM) using a JSM 5410-LV, JEOL. The elemental analyses of three TiO_2 samples were verified by Energy Dispersive X-ray Spectrometer (EDS). Specific surface area of all sample were measured by Surface Area and Pore Size Analyzer using Quadrasorb-EVO, Quantachrome with Brunauer-Emmett–Teller (BET) method. Particle size distribution of TiO_2-S, TiO_2-A, and TiO_2-P25 was measured by Zetasizer using Nano ZS, Malvern. The particle size was measured in range of 10 nm to 30 μm by dissolving the sample with water and sonication for 1 minute. The colloidal sample was put on sample cell and measured the particle size, and size distribution.

2. Study of the optimum condition for TiO_2 slurry preparation

Six types of pure solvent i.e. water (H_2O), propylene glycol (PG), dipropylene glycol (DPG), butylene glycol (BG), cyclomethicone (CMC), dimethicone (DMC) and nine types of mixed solvent in the ratio of 1:1, i.e. 1) PG and DMC, 2) PG and CMC, 3) DPG and DMC, 4) DPG and CMC, 5) BG and DMC, 6) BG and CMC, 7) PG and DPG, 8) PG and BG, and 9) DPG and BG were studied. In order to achieve the best result of suitable solvent for slurry preparation, 0.0075 g TiO_2 powder was added to each of 15 mL solvent and sonicated for 10 minutes. The optimum time of sonication was studied using 15 mL BG with 0.0075 g of TiO_2 powder and sonication time for 10, 20, 30, 40, 50, and 60 min. The optimum amount of TiO_2 powder was studied in various amounts of TiO_2 powder for 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 g with 10 mL of BG and sonication time for 30 minutes. The suitable source of TiO_2 powder was studied by using two sources of commercial TiO_2 powder (TiO_2-A and TiO_2-P25) and one source of synthesized TiO_2 (TiO_2-S) as the purpose of precursor using in TiO_2 slurry preparation instead of expensive commercial slurry. The texture properties of TiO_2 slurry from all conditions was studied compared with commercial TiO_2 slurry (Titasol S-35).

3. Preparation of sunscreen cream

Sunscreen cream was prepared from TiO_2 slurry of TiO_2-S compared with the sunscreen cream prepared from commercial Titasol S-35 followed in Table 1

Table 1 formula of sunscreen cream

Part	Materials	Weight (%)
A	Water	55.0
	Glycerin	3.0
	Amino Coat™	2.0
	Oligo GGF™	1.0
	Glydant Plus	0.35
B	Stearic acid	3.0
	E-wax	3.0
	Cethyl alcohol	3.0
	Shea butter	1.0
	Jojoba oil	1.0
	Caprylic Capric Triglyceride	2.5
	Cetiol OE	5.0
	Hostaphat KL340D	1.0
	TiO_2 slurry*, **	6.0
	Zincsol-S50	1.0
	Octylmethoxycinnamate	2.0
C	Cyclomethicone	5.0
D	Water	10.0
	Urea	2.0
E	Vitamin E	1.0

*Formula 1; TiO_2 slurry from commercial Titasol S-35
**Formula 2; synthesized TiO_2 slurry from this work

4. Stability test of sunscreen cream

Stability testing for two sunscreen cream formulas was based on protocols designed to test the cosmetic product attributes that are susceptible to change during storage. These attributes may influence cosmetic product quality, safety and performance. We evaluated product stability using freeze and thaw cycle (freeze and then thaw it out) for 6 cycles (Smaoui et al., 2017, pp. S1216–S1222) Appearance, odor, viscosity, texture and pH of sunscreen cream were also tested.

5. The volunteer's satisfaction test

Two formulas of sunscreen products were satisfaction tested by 40 volunteers who used both sunscreen creams that prepared from commercial Titasol S-35 and TiO_2 slurry from this work. Each formula of sunscreen cream was tested for one week. The satisfaction on sunscreen products was evaluated by questionnaire.

Results

TiO_2 powder was synthesized by microwave method and TiO_2 slurry was prepared by the optimum condition study. TiO_2 slurry was prepared from TiO_2-A, TiO_2-P25, and TiO_2-S. Results of this study were in Figure 1 TiO_2-A had peak pattern shows high intensity at 2θ = 24.8 and followed by 37.3, 37.81, 38.51, 47.99, 53.89, 55.07, 62.71, 69.0, 70.0, 75.0, respectively. TiO_2-P25 had peak pattern show high intensity at 2θ =24.8, and followed by 37.3, 47.99, 53.89, 55.07, 62.71, 69.0, 70.0, 75.0, respectively. TiO_2-S had high intensity peak at 2θ = 24.8, 27.31 and 29.0.

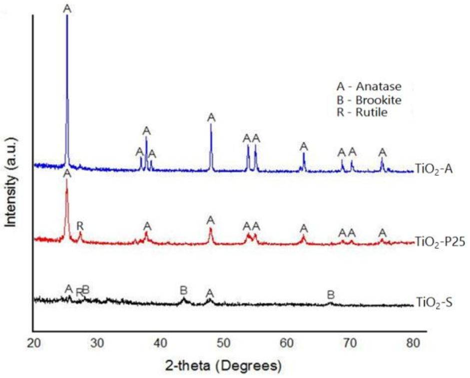

Figure 1 XRD patterns of TiO_2

TiO_2 powder was synthesized by microwave method and TiO_2 slurry was prepared by the optimum condition study. TiO_2 slurry was prepared from TiO_2-A, TiO_2-P25, and TiO_2-S. The morphology of TiO_2-A, TiO_2-P25, and TiO_2-S were observed by SEM at magnification of 5,000 and 10,000 as shown in Figure 2. The result shows that TiO_2-A and TiO_2-P25 show clouded of spherical shape, agglomerated particle, and roughness surface. TiO_2-S found that the particle size is larger size than TiO_2-A and TiO_2-P25, and forming a group of cubes with a shape that is apiece or a bar and a small scale mixed particles together.

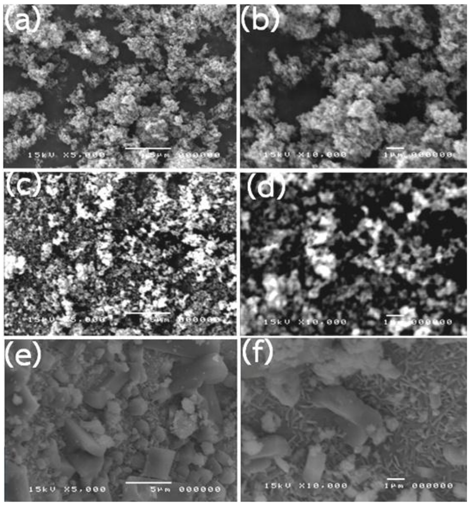

Figure 2 Morphology of TiO_2; (a) x5k of TiO_2-A, (b) x10k of TiO_2-A, (c) x5k of TiO_2-P25, (d) x10k of TiO_2-P25, (e) x5k of TiO_2-S, and (f) x10k of TiO_2-S

The particle size of TiO_2-A, TiO_2-P25, and TiO_2-S had particles size distribution around 90-700, 0.4-8, and 0.3-3 μm, respectively. The particles size in each range was calculated by program in zetasizer found that the particle size of TiO_2-A, TiO_2-P25, and TiO_2-S as shown in Table 2 The average particle size was evaluated of TiO_2-A, TiO_2-P25, and TiO_2-S as 0.297 μm, 8.427 μm, and 2.847 μm, respectively.

Table 2 Particles size of three TiO_2

No.	TiO_2-A (nm)	TiO_2-P25 (nm)	TiO_2-S (nm)
1	296.3	10,535.8	1,279.3
2	285.5	7,575,.8	3,065.9
3	290.2	7,172.4	2,509
Average	290.7	8,427.9	2,284.7

Specific surface area of TiO_2-A, TiO_2-P25, and TiO_2-S were measured by BET method. The results show that specific surface area of TiO_2-A, TiO_2-P25, and TiO_2-S was 56, 8, and 156.9 m^2/g, respectively.

The EDS spectrums showed that Ti and O were the main elements of TiO_2 powder for all TiO_2 samples as can be seen in Figure 3.

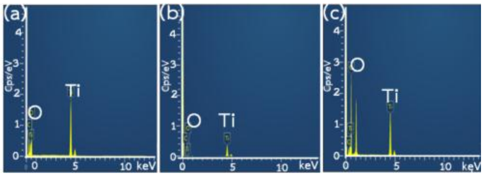

Figure 3 EDS spectrum of TiO_2; (a) TiO_2-A, (b) TiO_2-P25, and (c) TiO_2-S

Results of the suitable pure solvent study, the particles dispersion and precipitation after left for 5 days were observed. The dispersion occurred in H_2O, PG, DPG and BG, whereas separated of layer in DMC and CMC. After left at room temperature for 5 days, the precipitate can be seen in CMC > DMC > DPG > H_2O > PG > BG. (Figure 4). Due to low-molecular weight of CMC and DMC, dispersion of TiO_2 in that silicone oil needs polymeric dispersants for example, polyethylene glycol (Traiphol et al., 2013, pp. 315-321) Whereas, DPG, H_2O, PG, BG gave better results than CMC or DMC due to its high polarity. Nine Mixtures of medium; 1) PG and DMC, 2) PG and CMC, 3) DPG and DMC, 4) DPG and CMC, 5) BG and DMC, 6) BG and CMC, 7) PG and DPG, 8) PG and BG, and 9) DPG and BG were studied. It was found that PG mixed with BG gave the better result than other mixtures and it is similar result to single BG solvent. Even though, BG gave the best result in slurry form, it is expensive. Therefore, PG mixed with BG was chose as the medium for slurry preparation.

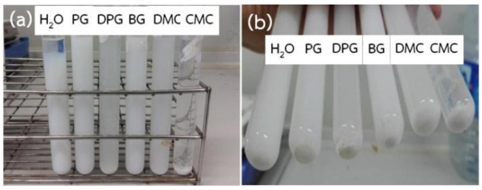

Figure 4 Sedimentation of TiO_2-S after sonication for 5 days; (a) layers, and (b) precipitate

The optimum time of sonication was studied to find the suitable time for sonication by varying as 10, 20, 30, 40, 50, and 60 minutes. The results showed that the precipitate decreased with increasing time of sonication. Due to ultrasonic wave has been proven as a useful tool to disperse nanoparticles and to eliminate agglomeration in aqueous suspensions. Precipitation of sample at 30 minutes shows the precipitate as little as 60 minutes. Therefore, time of sonication 30 minutes was selected as the optimum time.

The optimum amount of TiO_2 powder was studied in various amount of 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 g, with 10 mL of BG and PG (or 10, 20, 30, 40, 50, and 60% w/v) and sonication time for 30 minutes. Figure 5a show various amount of TiO_2 powder in 10 mL of BG and PG immediately after sonication. Figure 5b show various amount of TiO_2 powder in 10 mL of BG and PG immediately after sonication for 5 days. It was found that the optimum amount of TiO_2 as 60% w/v because of viscosity and flow rate of texture as same as commercial slurry, i.e. Titasol S-35.

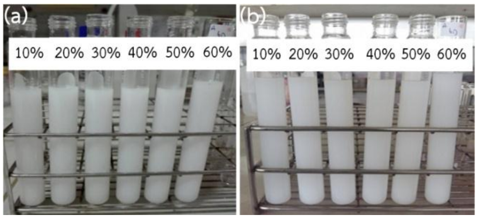

Figure 5 TiO_2-S in BG and PG; (a) immediately and (b) after sonication for 5 days

The suitable source of TiO_2 powder was studied by using three sources of TiO_2 powder that were commercial TiO_2-A, TiO_2-P25, and TiO_2-S. Each TiO_2 powder 12 g was dissolved in 20 mL BG and PG (60% w/v) with sonication time for 30 minutes. The result of slurry showed that TiO_2-A had homogeneous of white texture, TiO_2-P25 had heterogeneous of white texture but liquefied more than TiO_2-A and TiO_2-S. TiO_2-S, texture had homogeneous white-yellow color with viscosity as same as TiO_2-A. Therefore, TiO_2-A slurry was suitable for using in white cream, and TiO_2-S slurry was suitable for cream no need to be very white. On the other hand, TiO_2-P25 was not suitable for using in cream because of heterogeneous texture (see Figure 6)

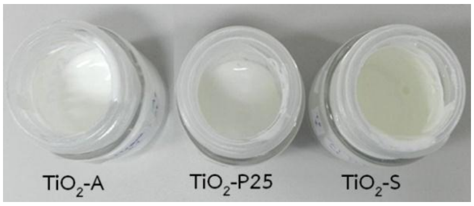

Figure 6 Texture of TiO_2-A, TiO_2-P25, and TiO_2-S slurry

The stability of TiO_2 slurry in both sunscreen creams was tested for 6 cycles by observing color, odor, viscosity, texture. The results showed in Table 3

Table 3 Properties of sunscreen cream

Property	Form. 1 (cream from Titasol-S35)	Form. 2 (cream from TiO_2 slurry)
Texture	homogeneous	homogeneous
Color	white	white-yellow
Odor	pleasant smell	pleasant smell
pH	6.0	5.8
Viscosity (cps)	35,846	35,267

The satisfaction on sunscreen products was evaluated by questionnaire. The results showed in Table 4 This table revealed that most volunteers prefer formula 2 that were prepared from TiO_2 slurry in this work (96 %) more than formula 1 (76 %). The reason, may be Titasol S-35 (commercial TiO_2 slurry) contains many ingredients, such as TiO_2, cyclopentasiloxne, PEG-10, dimethicone, aluminum hydroxide (and) stearic acid (Sinthai, 2018 p. 10) might that cause in sticky texture on skin when using.

Table 4 Satisfaction of volunteers on both sunscreen formulas

Satisfaction assessment criteria	Satisfaction level (5 point)	
	Formula 1	Formula 2
Color	3.80	3.95
Odor	3.70	3.75
Texture	3.70	4.40
Permeability into the skin	3.35	4.20
Moisturizing of the product	3.65	4.05
Feeling after applying	3.55	4.35
Average	3.63	4.80
Percentage	76.00	96.00

Conclusions and Discussion

TiO_2 slurry has been successfully prepared for easy use in cosmetics. Crystal structure of TiO_2-A had structure of anatase phase, TiO_2-P25 had structure mixed phase of anatase and rutile phase, and TiO_2-S after calcinations 700 $^{\circ}C$ for 2 hours shows small crystalnility of mixed phase of anatase, rutile and brookite. These results were correlated with the structure of anatase, brookite and rutile phase of TiO_2. The high intensity peak at 2θ = 24.8 referred to anatase, 2θ at 27.31 referred to rutile, and 2θ at 29.0 referred to brookite phase followed by JCPDS 29-1360 standard peak pattern of orthorhombic (Alkallas, Elshokrofy, & Mansour, 2019, pp. 1-7) The crystal structures of orthorhombic brookite (space group Pbca), tetragonal anatase (I41/amd), and tetragonal rutile (P42/mnm). The edge-sharing and corner-sharing TiO_6 octahedral were the more or less distorted trigonal planar environments of the oxygen atoms (Riedel, 2004, pp.71)

The morphology from SEM results show clouded of spherical shape and agglomerated particles of TiO_2-A and TiO_2-P25 because of the spherical of anatase phase (Kamitakahara et al., 2011, pp. 2283-2287) On the other hand, TiO_2-S, the particle size was larger size than TiO_2-A and TiO_2-P25, and forming a group of various shape and size may caused by mixed phase of anatase, brookite, and rutile. This result was related that TiO_2 has various particle shapes follow phase content and the condition of synthesis (García-López et al., 2019, pp. 118-124) Specific surface area of all TiO_2 from BET method shows that TiO_2-S has higher surface area than TiO_2-A and TiO_2-P25 (156.9, 56 and 8 m^2/g, respectively). Although particle size of TiO_2-S is bigger than the other, this is mixed phase of anatase, brookite and rutile. Thus this high surface area may be caused by pore between particles. In addition to having pore between each particle, there was also a pore between each phase, this enhance photocatalytic activity related with some report (Chang & Cho, 2019, pp. 683-693) The optimum solvent study for preparation of TiO_2 slurry show that the pure solvent is butylene glycol and mixed solvent is propylene glycol mixed with butylene glycol in ratio of 1:1. This result related the widely used cosmetic solvent (Veiga et al., 2018, pp. 261-271) The amount of TiO_2 as 60 % w/v was the optimum amount of TiO_2 for preparation of TiO_2 slurry because the viscosity and texture of TiO_2 slurry was same as commercial texture. The stability test of products, precipitation increased with increasing of the cycle number. The satisfaction of two formulas of sunscreen products exposed that most people like sunscreen prepared from this work for 96 %, this value is more than the commercial Titasol S-35.

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