DEVELOPMENT OF LIQUID CRYSTAL SUNSCREEN WITH DRAGON'S BLOOD EXTRACT

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ABSTRACT

Sunscreen has become essential for everyday life as it is important to keep your skin safe from UVA and UVB rays which can damage skin and cause many diseases especially if you are performing activities outdoors. The main objective of this study was aimed to determine the most suitable sunscreen formulation using liquid crystal characteristics to form new sunscreen formulations. One important property of the liquid crystals is preventing the fast release of the actives dissolved in the oil phase of an emulsion. This special characteristic of the lamellar liquid crystalline structure should provide the controlled-released ability for long lasting effect of the sunscreen and natural actives by preventing the fast release of the actives in the oil phase of an emulsion. Dragon's blood plant extract was also introduced into the formulation to boost the sunscreen performance against the sun radiation. The natural antioxidant agents from Dragon's blood extract play dominant roles in the radical scavenging and anti-inflammatory activities.

Six formulations (F1-F6) were prepared and the liquid crystal property was observed for its lamellar liquid crystalline transformation using the polarized optical microscope. We found that F3 and F4 with 5% Nikkomuless LC gave the good birefringence structure. All formulations were subjected to measured SPF values and obtained SPF ranged from 12.31 – 32.29. Furthermore, the plastic powder D-400HP in F 4 and F5 was loaded into the formulation as a physical sunscreen and the SPF values were 26.77 and 21.21, respectively which higher than F1 with no the plastic powder D-400HP. Formulation 2 and 4 had the same ingredients except for the amount of Nikkomuless LC and the SPF value was affect by the increasing of this ingredient. The amounts of Dragon's blood plant extract showed no significant affecting on the SPF value. In conclusion, formula 4 with good SPF value and good liquid crystal property was the best formulation in this study.

Keywords: Sunscreen, Liquid crystals, SPF, Plastic Powder, Dragon's Blood

1. Introduction

Sunscreen has become essential for everyday life regardless of sex and age, as it is important to keep your skin safe from UVA and UVB rays, especially if you are performing activities outdoors and sunbathing during the daytime. Since the advent of modern sunscreens, a sunscreen's efficacy has been measured by its sun protection

factor, or SPF. SPF indicates how long it will take for UVB rays to redden skin when using a sunscreen, compared to how long skin would take to redden without the product. There are currently 17 active ingredients approved by the FDA for use in sunscreens. These filters fall into two broad categories: chemical and physical. Most UV filters are chemical. They form a thin, protective film on the surface of the skin and absorb the UV radiation before it penetrates the skin. The physical sunscreens are insoluble particles that reflect UV away from the skin. (Morison & Wang, 2015)

Due to high hardness of physical inorganic sunscreen, it is sometimes difficult to achieve soft texture of the finished product. The Plastic Powder D-400 is composed mainly of very soft urethane resin. Therefore, they can provide remarkable soft texture and smooth feeling to the formulation. The spreadability of Plastic Powder D-400 is approximately 50 times higher compared to nylon powder, and the perfectly round shape of the particles adds to spread-ability, softness of the formulation, and provides light diffusing effect. (Toshiki International, 2014)

The theory of stabilizing an emulsion through the formation of a network of liquid crystals, the gelification of the water phase obtainable with hydrosolvatable polymers or with emulsifiers that are able to form a reticular organized structure in liquid crystal form, eliminates the need to use waxy components in large quantities and consistency factors that are no longer in harmony with the modern conception of light and easy to spread emulsions. (Arora, Agarwal, & Murthy, 2012).

Liquid crystals provide the following advantages to emulsion.

1) Stability: Emulsion stability of the multilayers around the oil droplets act as a barrier to coalescence. If oil droplets coalesce emulsion breaks, this barrier for coalescence acts as increased stability property of the emulsion. (Arora, Agarwal, & Murthy, 2012).

2) Prolonged hydration: Lamellar liquid crystalline and gel network contain water layer, which shows that 50% of the water of oil in water (o/w) emulsion can be bound to such structures. Such water is less prone to evaporation when applied to the skin and permits a long lasting moisture/ hydrating effect, necessary for drug entry. (Arora, Agarwal, & Murthy, 2012).

3) Controlled Drug delivery: Liquid crystals prevent the fast release of the drug dissolved in the oil phase of an emulsion. This is attributed to the lamellar liquid crystalline multilayer, which reduces the interfacial transport of a drug dissolved within the oil droplets. Microscopic observations under polarized light show the exceptional thickness of liquid crystalline lamellar layer around the oil droplets. (Arora, Agarwal, & Murthy, 2012).

Croton lechleri is a species of flowering plant in the spurge family. The plant is a medium-sized to large tree that grows from 10–20 meters high in the upper Amazon region of Peru, Ecuador, and Colombia. It has large, heart-shaped, bright-green leaves and unique, greenish-white flowers on long stalks. In Peru, its local name is Sangre de grado which is translated and widely known as “Dragon’s Blood”. For centuries, Dragon’s Blood has been used as traditional medicine in South America for its medicinal effect such as wound healings, anti-bacterial, anti-viral,

anti-inflammatory, anti-oxidant, anti-tumor, and anti-cancer. Dragon's blood resin is a combination of phytochemicals including proanthocyanidins, phenols, diterpenes, phytosterols, biologically active alkaloids and lignans. A number of scientific studies have confirmed the useful benefit of Dragon's Blood in wound healing or skin regeneration. "Dragon's blood has exceptional anti-inflammatory properties that have shown to stimulate human skin fibroblasts, which ultimately helps to heal the skin when marred by acne or injury (Taylor, 2013)". A clinical study on the efficacy of Dragon's Blood cream had also been conducted. "The study confirmed that after only 1 day of treatment with Dragon's blood, the wound contracts and a dark crust forms on the wound surface which prevents secondary infection. It also stimulated the proliferation and migration of fibroblasts and the production of collagen, resulting in epithelial regeneration and wound healing (Foroogh et al., 2014)".

2. Objectives of the study

In this research, the main objective was to develop an effective sunscreen formulation, combining the benefits of both chemical sunscreen and physical sunscreen including the employment of the Dragon's Blood, a powerful anti-oxidant natural extract, to achieve a high performance sunscreen in protection of the harmful sun rays

3. Materials and methods

The formulation of emulsions comprise of oil phase, aqueous phase and other components. Part A, or the oil phase, comprised of Nikkomulese LC from Nikkol (Japan), Nikkol Silblend 91 from Nikkol (Japan), NIKKOL DISM from Nikkol (Japan), NIKKOL Jojoba Oil from Nikkol (Japan), Cetostearyl Alcohol from Parchem (NY), Octyl Methoxycinnamate 0307 from Kyowa Hakko (Japan), Octocrylene from Kyowa Hakko (Japan), Butyl Methoxydibenzoylmethane from Kyowa Hakko (Japan), and Plastic Powder D-400HP from Toshiki (Japan). Part B, or the aqueous phase, consisted of deionized water, 1,3-Butylene glycol from Kyowa Hakko, (Tokyo, Japan), EDTA-2Na 0.10, Trisodium Citrate Dihydrate, and Citric Acid. Part C was deionized water and L-Arginine from CellMark (Singapore). Part D is the Dragon's blood extract.

For Sunscreen preparation, part A and part B were heated to 80°C respectively, then part A was added to part B. The mixture was kept homogenizing speed to 3500 rpm for 5 minutes. Then, part C was added at 70°C - 80°C with paddle and let it to cool down. Part D was added at 45°C and paddled it to finish off at 30°C. Repeat the same procedure for all formulas. (Nikko Chemicals Co., 2010)

Table 1 Liquid crystal sunscreen formulations

Liquid Crystal Sunscreen Ingredient Table	F - 1	F - 2	F - 3	F - 4	F - 5	F - 6
Part A						
NIKKOL Nikkomulese LC	3	3	5	5	10	10
Cetostearyl Alcohol	3	3	3	3	3	5
Nikkol Silblend 91	10	10	10	10	10	10
NIKKOL DISM	1	1	1	1	1	1
NIKKOL Jojoba Oil	0.5	0.5	0.5	0.5	0.5	0.5
Plastic Powder D-400HP	0	3	1	3	3	3
Octyl Methoxycinnamate	5	7	5	7	5	7
Octocrylene	2	4	2	4	2	4
Butyl Methoxydibenzoylmethane	1	3	1	3	1	3
Phenoxyethanol	0.9	0.9	0.9	0.9	0.9	0.9
Part B						
Ionized Water	Q.S to 100	Q.S to 100	Q.S to 100	Q.S to 100	Q.S to 100	Q.S to 100
EDTA-2Na 0.10	0.1	0.1	0.1	0.1	0.1	0.1
1,3-Butylene Glycol	5	5	5	5	5	5
Trisodium Citrate Dihydrate	0.6	0.6	0.6	0.6	0.6	0.6
Citric Acid	0.4	0.4	0.4	0.4	0.4	0.4
Part C						
L-Arginine	0.2	0.2	0.2	0.2	0.2	0.2
Water	2	2	2	2	2	2
Part D						
Dragon's Blood Extract	3	3	3	3	3	3
	100	100	100	100	100	100

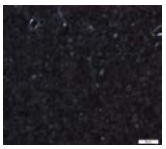
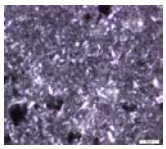
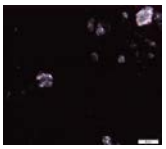
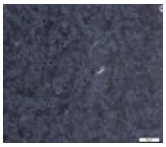
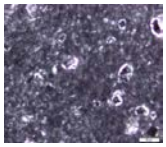
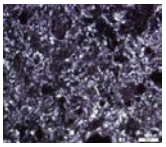
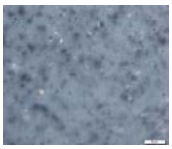
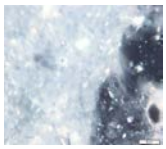
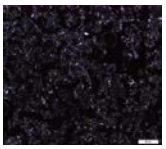
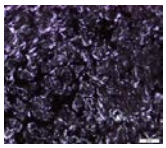
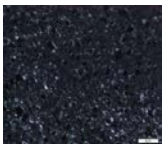
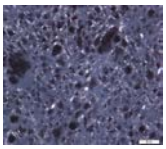
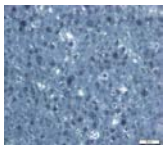
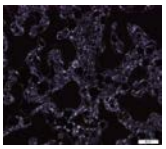
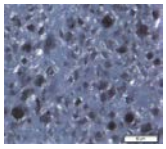
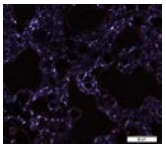
Determination of Liquid crystal structures: Pin-tip amount of the emulsion, and smeared onto the microscope glass slide, then quickly covered up by the cover slip. The sample needed to be finger pressed to make it as thin as possible. An objective lens and eye lens were used with cross polarizers in bright field to detect birefringence. The micrograph was taken under polarizing microscope at a different time for all formulations to observe the liquid crystal structure formation. (Zhang & Liu, 2013).

Determination of SPF Value: All liquid crystal sunscreen formulations (F1 – F6) were measured to determine their SPF Value using the Optometrics SPF-290S. The liquid crystal sunscreen sample was applied in small spots with the syringe over a 50 cm^2 area at 2 ml/cm^2 on the Transpore Tape, then it was placed on an open metal frame. The liquid crystal sunscreen spot was spread lightly and uniformly across the surface area. The sample was kept in the dark for 15 min. The SPF measurement was performed on Optometrics SPF-290S analyzer. Initially, the blank Transpore Tape was measured, and the data was collected. Then, the sample was measured in six different points and the data were analyzed for SPF, UVA/UVB ratio. (Piyapong Choochana, et al., 2015).

4. Results

Six formulations (F1-F6) were prepared and the liquid crystal property was observed for its lamellar liquid crystalline transformation using the polarized optical microscope (Table 2).

Table 2 Liquid Crystal Structure Observation Result

Number	Time 1 Apply Sunscreen - 0 hour	Time 2 1 hour	Time 3 3 hours
Formulation 1			
Formulation 2			
Formulation 3			
Formulation 4			
Formulation 5			
Formulation 6			

All six formulations were subjected to viscosity measurement (Scott Low Range Viscometer 110, USA) and the results were shown on table 3. All liquid crystal sunscreen formulations (F1 – F6) were measured to determine their SPF Value using the Optometrics SPF-290S (Table 4).

Table 3 Liquid Crystal Sunscreen Viscosity Measurement Result

Formulation	Viscosity (cP)
F1	2290
F2	2450
F3	3110
F4	2371
F5	2885
F6	>6000

Table 4 Liquid Crystal Sunscreen Formulations SPF Test Result

Formulation	SPF	UVA/UVB ratio	Boot's star Rating
F1	12.31 ± 4.55	0.610	2 (Moderate)
F2	23.82 ± 9.78	0.860	4 (High)
F3	19.1± 6.38	0.620	2 (Moderate)
F4	26.77 ± 8.39	0.820	3 (Good)
F5	21.21 ± 4.55	0.630	2 (Moderate)
F6	32.29 ± 10.71	0.800	3 (Good)

5. Discussion

Six formulations (F1-F6) were made as the oil in water emulsion and the liquid crystal property was observed for its lamellar liquid crystalline transformation using the polarized optical microscope. The liquid crystal was observed right after prepared, 1 hour, and 3 hours later for stability determination of liquid crystal property. From the result, F3/F4/ and F5 had demonstrated a good formation of liquid crystal structures. Moreover, F4 had shown the best liquid crystal structures which remained present until the observation at 3 hours later. This special liquid crystalline structures helped encapsulate the sunscreen actives and preventing the fast release of the actives dissolved in the oil phase; in this manner, the crystalline structures exhibit the controlled-released characteristic which helped prolong the actives and their sunscreen effect

For the viscosity of the formulations, F6 had the highest viscosity because of high content of Nikkomuless LC and cetostearyl alcohol. F3 and F5 which had nearly composition showed the same range of viscosity from 2885 to 3110 cP. In addition, F2 and F4 were also demonstrated the same phenomenon.

For SPF measurement, we obtained SPF ranged from 12.31 – 32.29. Furthermore, the plastic powder D-400HP in F4 and F5 was loaded into the formulation as a physical sunscreen and the SPF values were 26.77 and 21.21, respectively which higher than F1 with no the plastic powder D-400HP. Formulation 2 and 4 had the same ingredients except for the amount of Nikkomuless LC and the SPF value was affect by the increasing of this ingredient. Formula 4 showed good SPF value, high UVA/UVB ratio and good liquid crystal property. The amounts of Dragon's blood plant extract showed no significant affecting on the SPF value.

6. Conclusion

In conclusion, we obtained a good formula which was F4 that had good SPF value, high UVA/UVB ratio and good liquid crystal property. This formula is the best formulation in this research, which composes of desired characteristics for good sunscreen and should be subject to a further study in physical and chemical stability.

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References

Arora, N., Agarwal, S., Murthy, R.S.R. (2012). Latest Technology Advances in Cosmaceuticals. Retrieved November 15, 2016, from International Journal of Pharmaceutical Sciences and Drug Research. Website : http://www.ijpsdr.com

Foroogh N. A., Fatemeh K. B., Zahra B. M., Fatemeh S. B. , Behzad S. M. (2014). Efficacy of Dragon's blood cream on wound healing: A randomized, double-blind, placebo-controlled clinical trial. Journal of Traditional and Complementary Medicine 6, 37 – 40 (2016).

Morison, W. L., Wang, S. Q. (2015, November), Sunscreen: Save and Effective? Skin Cancer Foundation. Retrieved January 20, 2017, from http://www.skincancer.org/prevention/sun-protection/sunscreen/sunscreens-safeand-effective.

Nikko Chemicals Co., Ltd, Colloid Science (2010). Emulsifier for liquid crystal System. Retrieved February 15, 2017, from http://www.nikkol.co.jp/en/research/colloid-science.html

Piyapong Choochana, Jirapan Moungjaroen, Nathjanan Jongkon, WandeeGritsanapan & Prasan

Tangyuenyongwatana (2015). Development of piperic acid derivatives from Piper nigrum as UV protection agents, Pharmaceutical Biology, 53:4, 477-482

Toshiki International (2014). Product Information : Plastic Powder Series [Brochure] Retrieved March 5, 2017, from http://www.in-cosmetics.com/__novadocuments/7995

Taylor, L. (2013, February), Tropical Plant Database. Retrieved March 5, 2017, From http://www.rain-tree.com/sangre.htm

Zhang, W., Liu, L. (2013). Study on the Formation and Properties of Liquid Crystal Emulsion in Cosmetic. Journal of Cosmetics, Dermatological Sciences and Applications, 3, 139-144