Environmental Benefit of Applying Polyglycerol Emulsifiers in Sun-protective Formulation

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Abstract (Maximum of 250 words)

Background: Sun-protected products are facing increasing challenges today by the regulation restrictions and the consumer demand for higher performance. In this study, using 100% natural polyglycerol-based emulsifier, two approaches were provided to address the current challenges of complying with the regulatory restrictions, while increasing SPF boosting ability, and enhancing the water-resistant ability of formulation.

Methods: The in vitro SPF and water resistance retention (WRR%) measurement methods were used to compare traditional PEG-based emulsifier with various types of natural polyglycerol emulsifiers. The mechanisms of SPF boosting and improvement of water resistance retention were investigated through observing liquid crystal emulsion by using polarized micrograph, and multi-emulsion phenomenon by optical micrograph.

Results: For SPF boosting, polyglycerol-based emulsifier formulations provide SPF at least 1.5 times higher than that of PEG-based emulsifier formulation due to the lamellar liquid crystal formation. The results were also verified by moisture-increment measurement data and time-dependent SPF-lamellar liquid crystal emulsion relationships, and further demonstrated SPF value boosting by the presence of interlamellar water. In terms of water-resistant ability, polyglycerol-based emulsifier formulaitoins provide about 2-3 times of WRR% than that in PEG-based emulsifier formulation. Furthermore, formulation contained polyglyceryl-10 laruate emulsifier paried with polyglyceryl-2 triisostearate co-emulsifier is easily forming W/O/W multi-emulsion and provides the great improvement in WRR%.

Conclusion: The polyglycerol-based emulsifier and co-emulsifier have been proven suitable for using in high-performance environmentally friendly sun protection formulations. The test results show that UV-filter SPF 30 has been boosted to SPF 50+, and water resistance retention has been improved from 13.6% to 75.8%.

Keywords: Polyglycerol emulsifier; SPF booster; Water resistant retention; Eco-friendly; Lamellar liquid crystal emulsion; W/O/W multi-emulsion

Introduction

UV-filters are specific compounds that block the passing of UV light, generally classified as either chemical UV-filters (absorbing UV light) or physical UV-filters (scattering and absorbing UV light) [1], are widely used in consumer cosmetics industry. In personal care and cosmetics, UV-filters are applied to stabilize formulations or protect skin from sun damage. To avoid photoaging and sunburn [2], today's consumers put more and more attention on sun-protective products, making it an important field in cosmetic industry. However, it is never an easy task to formulate a perfect sun-protective product. Additionally, the dosage amount had been limited by regulations among different countries [3,4], and some recent studies have indicated that UV-filters may cause ocean pollution and impact ocean ecology [5]. As such, it is a real challenge for formulators to meet all the needs of customers, while maintaining eco-friendly aspect. In other words, it is a trade-off between reducing UV-filter dosage to meet the regulations and keeping certain sun protection ability. That is why SPF boosters are worthy of investigating and being applied to sun-protective formulations.

Traditionally, SPF boosters are emollients or polymers that can boost the effect of chemical UV-filters by efficiently dissolving it into formulations [6]. Nowadays, the function of SPF boosters is no longer limited to dissolving higher concentration of UV-filters. Other functions are also taken into consideration, such as improving the photostability of UV-filters [7-9], increasing the optical path length [7,10,11], or optimizing the film-forming properties during spreading [7,12].

From the perspective of environmental protection, it is very important to reduce the risk of releasing UV-filters into the environment. During water activities, the sun-protective products are sometimes easy to wash off by the water and lead to the decrease of sun-protective ability. In order to maintain the protection ability, users need to reapply the products frequently, this action eventually rises the risk of releasing greater amount of UV-filter into the environment. By increasing the water resistance ability of sun-protective products, we can effectively avoid this kind of situations happening, and significantly reduce the possibility of polluting the environment.

Polyglycerol-based emulsifiers are surfactants formed by esterification of polyglycerol and fatty acid. The HLB of polyglycerol-based emulsifiers are affected by the polymerization degree of polyglycerol, chain length of fatty acid, and esterification degree. In the previous study, the polyglycerol-10 ester had been applied to sun-protective formulation and exhibited good UV-filter solubility. In that formulation, it led to formation of small size micelle, and boosted the SPF value [13]. Moreover, water-resistant ability improved by using polyglycerol-10 ester was also reported [14]. However, such enhancement was shown only in the formulation paired with polymer additive, there was no data for formulation using polyglycerol-10 ester alone.

This paper demonstrates the environmental benefits of using polyglycerol ester emulsifiers in sun-protective formulations. The SPF boosting and water-resistant ability of various type of polyglycerol emulsifiers are compared with the traditional PEG-based emulsifier. To further understand the mechanisms of SPF booting and the water resistance ability of polyglycerol ester as emulsifier and co-emulsifier, the results of the polarized micrograph, optical micrograph, and moisture-increment measurement are discussed. Based on the results, the polyglycerol-based emulsifiers, and co-emulsifiers are proven to be the great options for eco-friendly sun-protection formulations.

Materials and Methods

2.1. Prepare the Formulations

In order to measure the SPF, water resistance retention, and observe microscopy phenomenon, the formulations F-1~F-8 shown in Table 1 were prepared. For all formulations, all ingredients in phase A and phase B were mixed at 80°C individually. The well-mixed phase A was added into phase B slowly under continuous stirring. Subsequently, the mixture was homogenized at 5000 rpm for 5 minutes by a homogenizer. Afterwards, the mixture cooled down to 40°C under gentle stirring.

In these formulations, the ingredient Butyl methoxydibenzoylmethane and Ethylhexyl methoxycinnamate were purchased from BASF, Titanium dioxide was purchased from Tayca corporation, Polysorbate 85 was purchased from Croda, Cetearyl alcohol was purchased from Sinarmas, and Glycerin was purchased from IOI Oleochemical. The polyglycerol esters and emollients, such as Polyglyceryl-10 laurate, Polyglyceryl-4 laurate, Polyglyceryl-4 caprate, Polyglyceryl-2 isostearate, Polyglyceryl-2 diisostearate, Polyglyceryl-2 triisostearate, C12-15 alkyl benzoate, Isononyl isononanoate, Caprilic/Capric triglyceride, were all provided by Patech Fine Chemicals Co., Ltd.

Table 1 The formulations for tested in this study

	INCI Name	F-1	F-2	F-3	F-4	F-5	F-6	F-7	F-8
Phase A	Butyl methoxydibenzoylmethane	2	2	2	2	2	2	2	2
	Ethylhexyl methoxycinnamate	4	4	4	4	4	4	4	4
	Titanium dioxide	6	6	6	6	6	6	6	
	C12 -15 alkyl benzoate	5	5	5	5	5	5	5	5
	Isononyl isononanoate	5	5	5	5	5	5	5	5
	Caprilic/Capric triglyceride	5	5	5	5	5	5	5	5
	Polysorbate 85	4.2	-	-	-	-	-	-	-
	Polyglyceryl-10 laurate	-	4.2	-	-	4.2	4.2	4.2	4.2
	Polyglyceryl-4 laurate	-	-	4.2	-	-	-	-	-
	Polyglyceryl-4 caprate	-	-	-	4.2	-	-	-	-
	Cetearyl alcohol	2.8	2.8	2.8	2.8	-	-	-	2.8
	Polyglyceryl-2 isostearate	-	-	-	-	2.8	-	-	-
	Polyglyceryl-2 diisostearate	-	-	-	-	-	2.8	-	-
	Polyglyceryl-2 triisostearate	-	-	-	-	-	-	2.8	-
Phase B	Water	62.2	62.2	62.2	62.2	62.2	62.2	62.2	68.2
	Glycerin	3	3	3	3	3	3	3	3
	Xanthan gum	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
	Preservative	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5

2.2. In vitro SPF measurement

SPF value measurement was conducted by applying the formulation on standard PMMA plate (Schonberg), placing the PMMA plate in a dark area for 15 min, then measuring by UV-2600i spectrometer (Shimadzu). All the SPF measurement procedure, parameters and calculation were according ISO 24443:2012.

2.3. Water resistance retention

The water resistance ability was evaluated by water resistance retention (%WRR), which was calculated by eq.1 [15] .

$$WRR(\%) = \frac{SPF_{iw}-1}{SPF_{is}-1} \times 100\ \% \qquad \text{Eq. 1}$$

The SPF_{iw} is SPF after water immersion test and the SPF_{is} is SPF before water immersion test. Initially, the formulation was applied on the PMMA plate, and obtained the SPF_{is} according to the measurement procedure describing in section 2.2. Afterwards, formulation-coated PMMA plates were immersed in 3L water and stirred under 500rpm for 15 minutes. After removing residual water drops on the PMMA plate, SPF_{iw} can be measured.

2.4. Polarized light microscope and optical microscope measurement

In order to observe the lamellar liquid crystal emulsion, the microscopy (Hamlet MH146) equipped with two polarizers, above and below the sample stage at 90-degree angle, was used (polarized light microscope). For multi-emulsion phenomenon observation, remove the polarizers, and directly conduct this measurement (optical microscope).

2.5. Moisture test

According to literature [16], the lamellar liquid crystal emulsion structures are separated and stabilized by interlamellar water. In order to verify the relationship between lamellar liquid crystal emulsion and moisture content after applying on the skin, the formulations F-1 and F-2 were applied to the forearm respectively. After that, we recorded the moisture value of blank region and applied area region at 0, 0.5, 1, 2, 3, and 4 hours. The moisture increment was calculated by Eq. 2. The M_f and M_b are moistures of formulation on applied region and blank region respectively.

$$Moisture\ increment(\%) = \frac{M_f - M_b}{M_b} \times 100\% \qquad \text{Eq. 2}$$

Results

3.1. Emulsifier and co-emulsifiers effects on SPF value and water resistance retention

The SPF value and water resistance retention of formulation F-1~F-7 are presented in Table 2. Regarding SPF value results, formulation F-1~F-4 can be used as different emulsifier type effect comparison under the same co-emulsifier. F-1 is the formulation containing a PEG-based emulsifier. F-2, F-3, and F-4 contain different polyglycerol-based emulsifiers, polyglyceryl-10 laurate, polyglyceryl-4 laurate, and polyglyceryl-4 caprate, respectively. The results indicate SPF using polyglycerol-based emulsifier are all around 45-50, and provide a significant SPF boosting ability compared with PEG-based emulsifier formulation. Besides, F-2, F-5, F-6, and F-7 can be used as different co-emulsifier type effect comparison under the same emulsifier, polyglyceryl-10 laurate. The paired co-emulsifiers in these formulations are cetearyl alcohol, polyglyceryl-2 isostearate, polyglyceryl-2 diisostearate, and polyglyceryl-2 triisostearate respectively. The result shows, polyglyceryl-2 triisostearate (F-7) is more superior compared to the other co-emulsifiers in formulation SPF boosting effect.

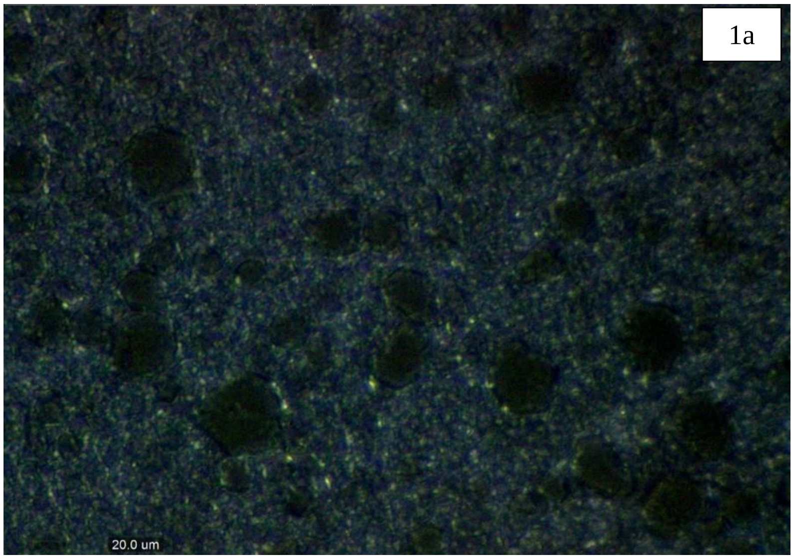
When it comes to the water resistance retention, formulation F-1~F-4 WRR% results show that polyglycerol-based emulsifier formulations can provide nearly two to three times of water resistance retention compared to PEG-based emulsifier formulations. In addition, co-emulsifiers types play a key factor in WRR% for polyglyceryl-10 laurate emulsifier formulations. Compare F-2, F-5, F-6, and F-7, as a co-emulsifier, polyglyceryl-2 triisostearate (F-7) is superior than traditional co-emulsifier cetearyl alcohol (F-2) in WRR%, but polyglyceryl-2 isostearate (F-5) and polyglyceryl-2 diisostearate (F-6) are inferior than cetearyl alcohol (F-2).

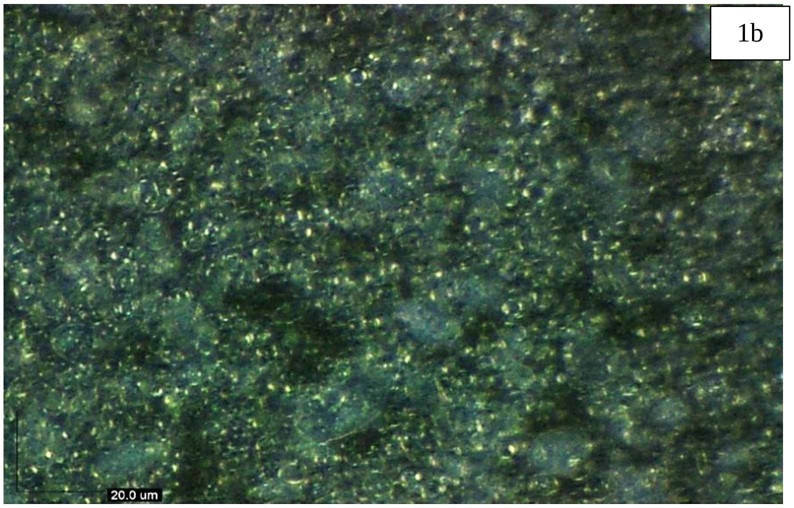
Table 2. The SPF and water resistance retention for different type of emulsifier and co-emulsifier

	F-1	F-2	F-3	F-4	F-5	F-6	F-7
SPF value	30.4	47	46.1	49	46.9	45	59.8
WRR (%)	13.6	38.4	34	30.2	13.1	13.9	75.8

3.2. The polarized light microscopy observation

To understand the mechanism of SPF boosting, we compare the difference between of F-1 and F-2 through polarized light microscopy observation, shown in Fig. 1. In the polarized light micrograph of the polyglyceryl-10 laurate formulation (F-2, Fig. 1b), the brightness around the micelle could be observed, it is different from the image of Polysorbate 85 formulation (F-1, Fig 1a). The Fig. 1c shows the partially magnified image of Fig 1b. In this figure, the Maltese cross could be observed clearly which often appeared in the polarized light micrograph of lamellar liquid crystal emulsions.





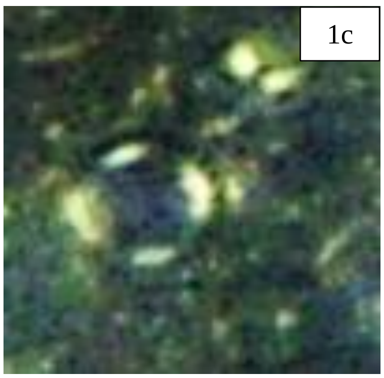


Fig. 1 The polarized light micrograph of (a) the formulation F-1 (b) the formulation F-2 (c) Maltese cross of Liquid crystal in the image of formulation F-2

3.3. Time-dependent SPF-lamellar liquid crystal relationship

To further clarify the relationship between lamellar liquid crystal formation and SPF value, the SPF and polarized light micrograph at the different aging times of formulation F-8 were determined. Table 3 presents the SPF values in aging time on day 0, day 2, and day 4, and it is clear that SPF increases with aging time. The polarized light micrographs of different aging time are presented in Fig. 2., and the comparison of these images with time clearly show that the Maltese cross image is generated on the fourth day.

Table 3 The F-8 formulation SPF of the different aging times

	Day 0	Day 2	Day 4
SPF	12.6	14.7	18.6

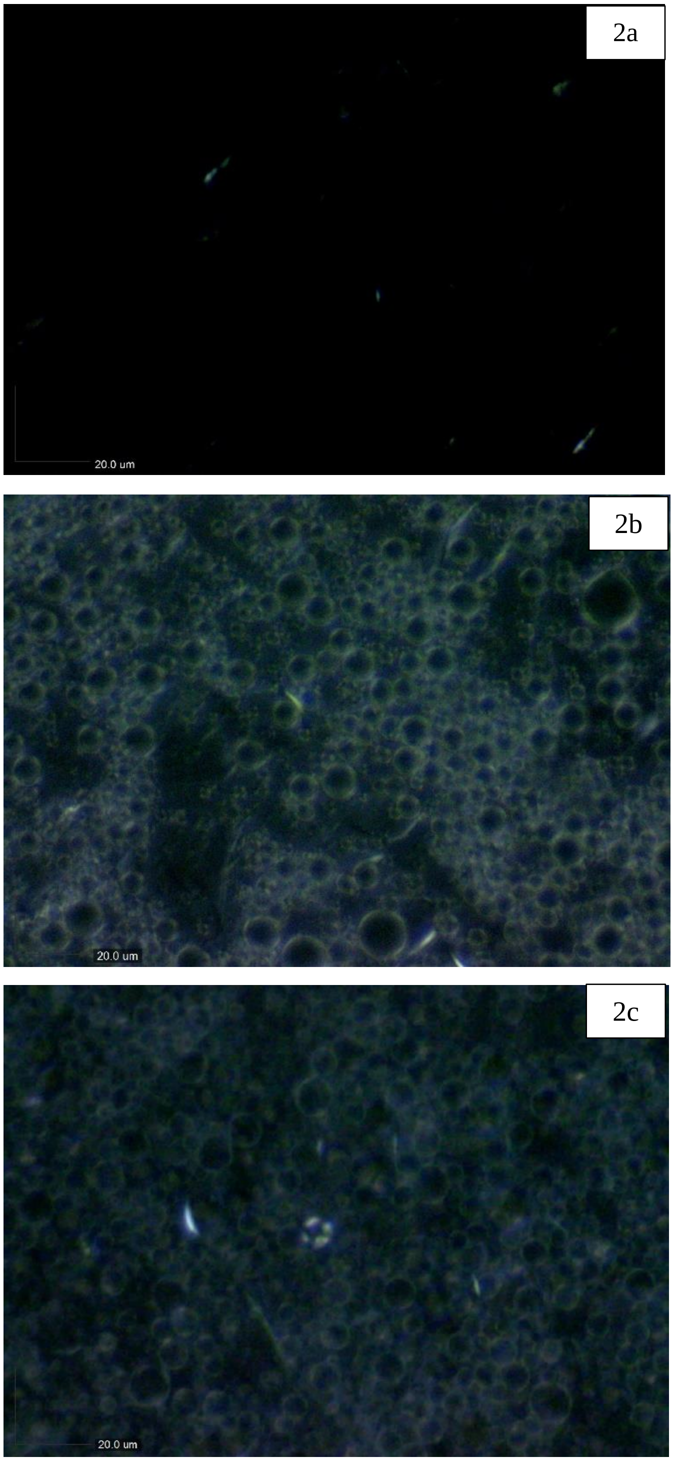


Fig. 2 The polarized light micrograph of (a) day 0 (b) day 2 (c) day 4

3.4. Moisture content of formulation using polyglyceryl-10 laurate and Polysorbate 85

The moisture increments by formulation F-1 and F-2 after being applied is presented in Fig. 3. Based on the results, F-2 provides a significant higher moisture increment than F-1 within 4 hours.

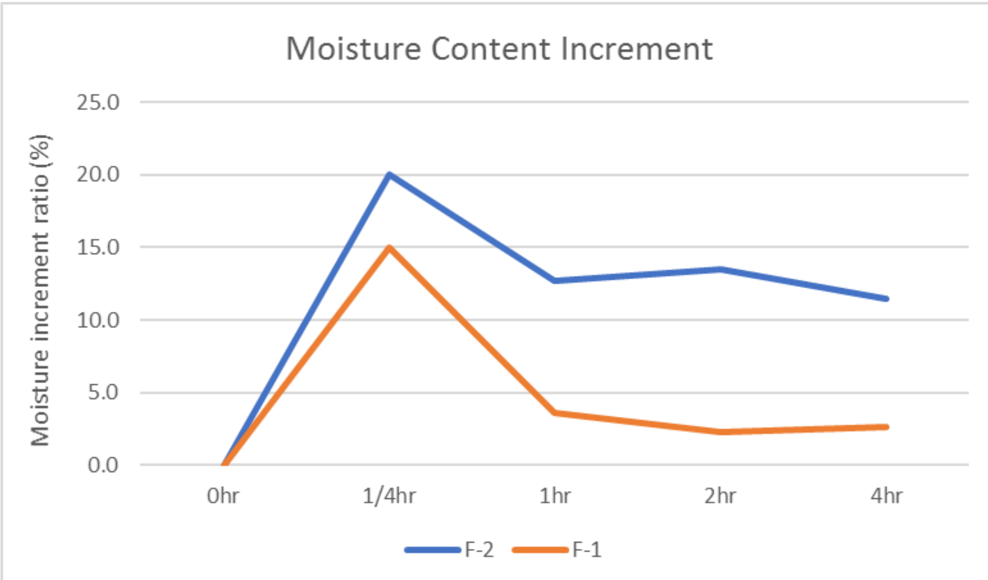
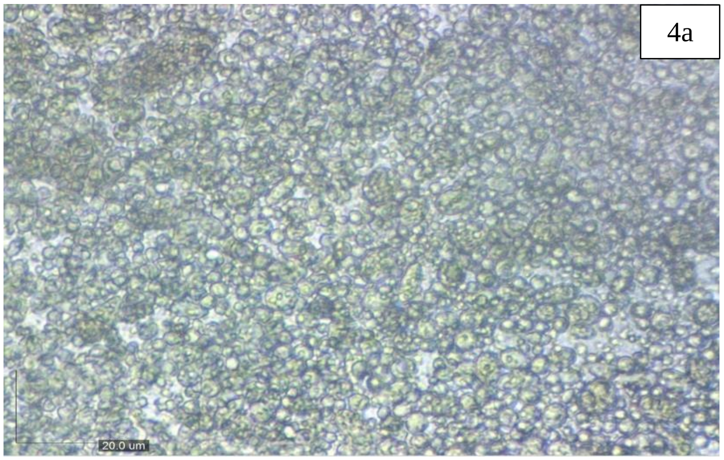


Fig. 3 Skin moisture increment ratio by applied formulations F-1 and F-2

3.5. The optical microscopy observed of micelle

In order to understand the possible reasons for the difference WRR% by using different co-emulsifiers, the optical micrographs of formulation F-2~F-7 were observed. The results are presented in Fig. 4, and it is easy to find that the W/O/W mufti-emulsion formation in both Fig.4a (F-2) and Fig.4f (F-7). Further comparison shows that formulation F-2 appear only few micelles formed W/O/W multi-emulsion in the upper left corner, but there are more apparent W/O/W multi-emulsion phenomenon in F-7. On the other hand, the micrograph of formulation F-3~F-6 (Fig.4b~ Fig.4e) show only normal micelles, without any W/O/W multi-emulsion formation.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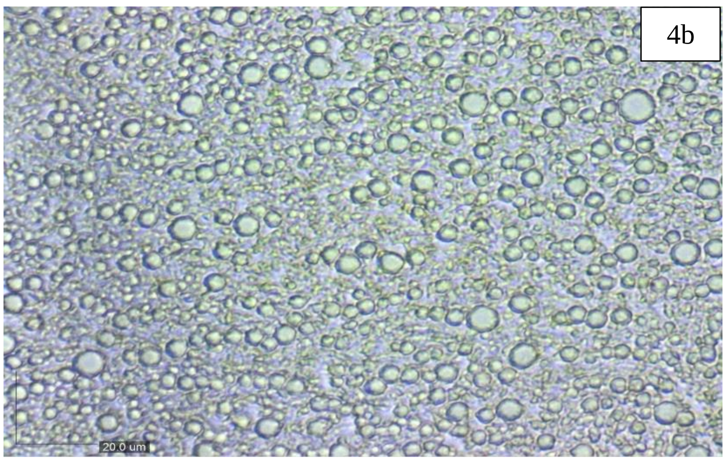
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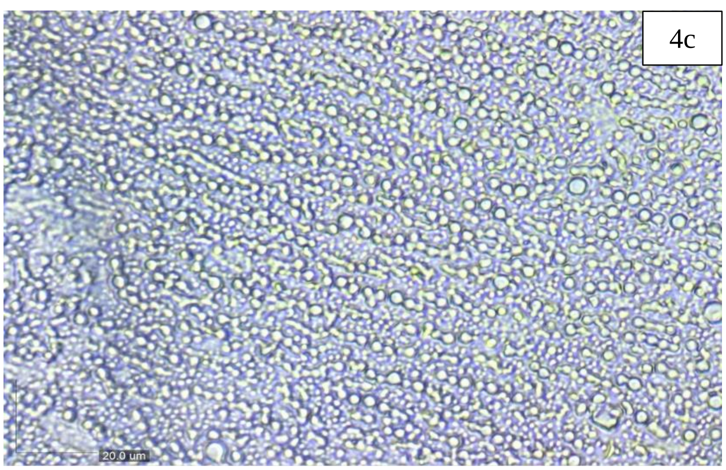
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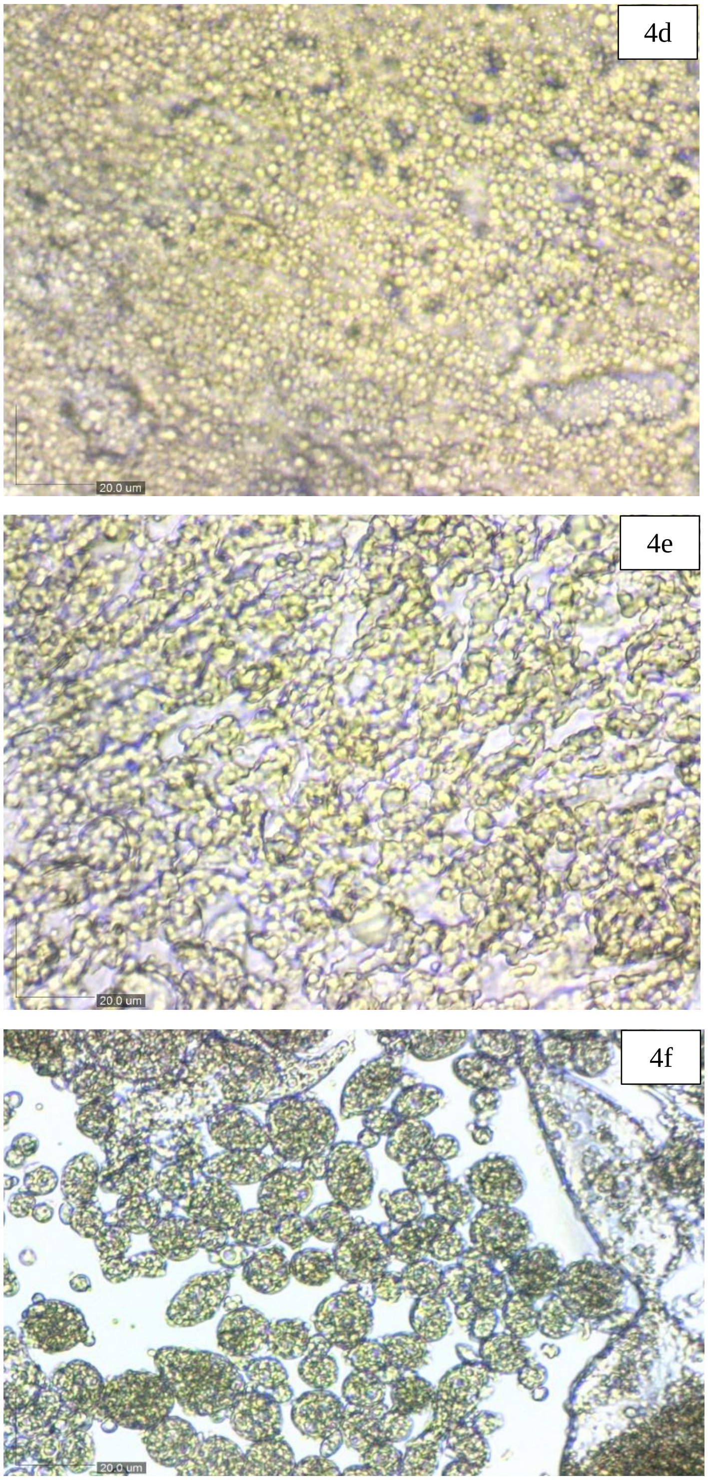

Fig.4 The optical micrograph of (a)formulation F-2 (b)formulation F-3 (c)formulation F-4 (d)formulation F-5 (e)formulation F-6 (f)formulation F-7

Discussion

In the SPF boosting study, formulations F-1~F-4 using different type of emulsifiers were compared. All of the polyglycerol-based emulsifiers impart a similar boosting ability for at least 1.5 times higher than traditional PEG-based emulsifier. In the polarized light microscopy observations, phenomenon of lamellar liquid crystal formation only appears in formulation F-2, but not in F-1. Furthermore, the time-dependent polarized light microscopy data show that it takes times for the formation of liquid crystal in F-2 emulsion formulation. To clarify the moisture content effect on lamellar liquid crystal stability, moisture-increment of formulation F-1 and F-2 were measured and appeared different results. Comparison of different type of co-emulsifiers shows that formulation F-7 is superior than the other co-emulsifiers in formulation SPF boosting effect (F-2, F-5, and F-6).

Turning to water resistance retention results, in formulations F-1~F-4, all the polyglycerol-based emulsifier formulations show 2-3 times of WRR% than that in PEG-based emulsifier formulation. Regarding co-emulsifier effect (F-2, F-5, F-6, and F-7), different type of co-emulsifiers shows different effects on WRR%. The mechanism can be further verified by optical microscopy observation results and literature survey.

4.1. SPF boosting ability

This study has already verified that various type of polyglycerol emulsifiers impart a better SPF boosting ability than traditional PEG-based emulsifier, and similar results have also been mentioned in the literature [13]. The literature argued that the SPF boosting ability comes from the small size micelle to make the uniform coating on the skin. However, emulsion is a thermodynamically unstable system, therefore the micelles may aggerate and thereby form larger micelle during the flocculation process with time. Specifically, SPF should be decreased within a long-time test if micelles aggerating happened. Our time-dependent experimental results of section 3.3 show that SPF is increased with the formation of lamellar liquid crystal of emulsion, and reached the highest SPF after the Maltese cross pattern appeared (4 days test). There are no enough evidences in our experiment for discussion of SPF value maintaining or decreasing during longer time observation (more than 4 days). But since liquid crystal can extend the period of small micelles stabilization[17,18], it may lead the formulation to keep at high SPF value for a long time.

Although the experimental results of section 3.3 can contribute the relationship between SPF and lamellar liquid crystal emulsion formation, the mechanism of SPF boosting by lamellar liquid crystal emulsion formation has not been verified. Interlamellar water concept by Goodby et al. [16] could be taken for explanation. According to literature, the lamellar structures are separated and stabilized by water, which is called interlamellar water. To further understand how interlamellar water increases the SPF boosting ability, the basic optics theory should be reviewed. The Snell–Descartes law [19] described refraction phenomena as presenting by light passing through a boundary between two different media. In the lamellar liquid crystal structure, the lamellar-structure and interlamellar water provide the condition to enhance the light refraction, and increase optical path length to act as SPF booster [7,10,11]. Our results in section 3.2 and section 3.4 prove that formulation with higher moisture-increment is tend to form more liquid crystal structure, afterwards lead to SPF boosting effect.

4.2. Water resistance retention

In section 3.1, test results show that there is no significant relationship between the tendency of water resistance retention and SPF boosting ability. However, the co-emulsifier type imparts a certain effect on the water resistance retention, as shown in Fig. 5, and the tendency is that co-emulsifiers with lower hydroxyl value (non-polar) provide the higher water resistance retention. In order to understand possible mechanisms of water resistance retention, the optical micrographs of formulation F-2~F-7 are investigated. The W/O/W multi-emulsion phenomena are observed in the formulations F-2 and F-7 which are owing higher water resistance retention. Furthermore, comparing the optical micrographs of formulation F-2 and F-7, the higher W/O/W multi-emulsion concentration in F-7 leads to higher water resistance retention than that in F-2. The water resistance retention affected by W/O/W multi-emulsion was also reported by Lee et al. [20], and similar results were also argued. This phenomenon can be explained as following concept: W/O/W contains more oil-water interfaces to share emulsifier, therefore the emulsifier concentration between oil-water interface in W/O/W multi-emulsion is lower than that in the water-oil interface in O/W emulsion. The lower concentration of emulsifier will lead the oil phase more difficult to be removed by water during the water washing process, and then enhance WRR%.

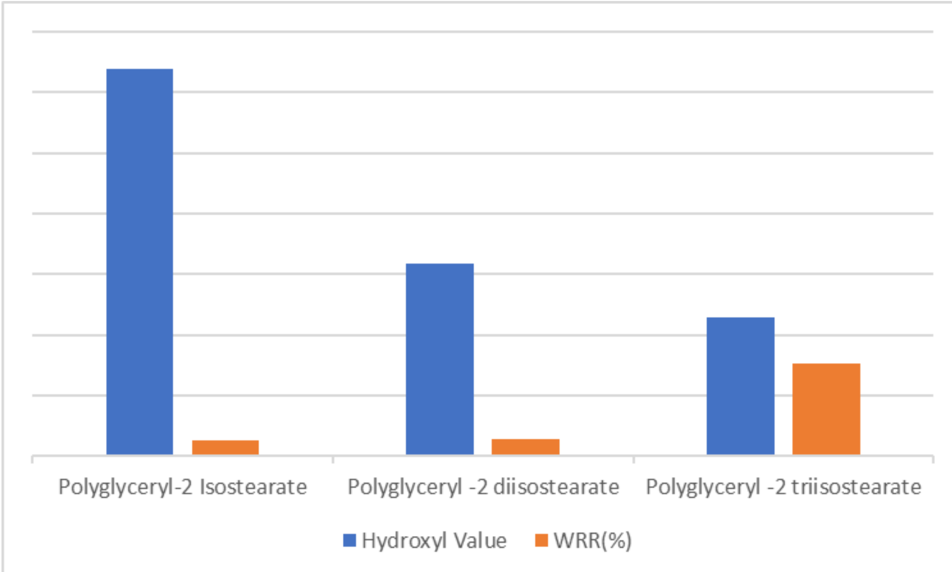

Fig. 5 The tendency of the hydroxyl value of co-emulsifier and WRR(%)

4.3. Environmental benefit of polyglycerol-based emulsifier

Due to environmental concerns, UV-filters dosages are regulated because of their hazards to marine organisms. Consequently, the industry is striving to achieve the highest SPF in the formulation using the lowest amount of UV-filter. In section 3.1, the UV-filter performance of SPF 30 is boosted by the emulsifier polyglyceryl-10 laurate paired with the co-emulsifier polyglyceryl-2 triisostearate to achieve SPF 50+. On the other hand, the emulsifier polyglyceryl-10 laurate paired with the co-emulsifier polyglyceryl-2 triisostearate also improves the water resistance retention from 13.6% to 75.8% via W/O/W multi-emulsion formation. The sun protection products with high water resistance retention can lower the frequency of reapplying the products and reduce the risk of UV-filters entering the environment during water activities.

Conclusion.

This study has verified the SPF boosting ability of various polyglycerol-based emulsifiers compared with traditional PEG-based emulsifier. The mechanism of SPF boosting by the formation of lamellar liquid crystal has been proved via polarized micrographs and the time-dependent SPF-lamellar liquid crystal relationship. Regarding the water resistance retention study, the formulation containing polyglyceryl-10 laurate paired with polyglyceryl-2 triisostearate improves the water resistance retention significantly due to the formation of W/O/W multi-emulsion. The various polyglycerol-based emulsifiers and co-emulsifiers show significant SPF boosting and great water resistance ability in the sun protection formulation, the UV-filter performance of SPF 30 has been boosted to SPF 50+ and water resistance retention is increased from 13.6% to 75.8%. The lower dosage of UV-filters and higher water resistance ability both can reduce the risk of UV-filters entering the environment, in addition, reduce the impact on ecology, especially marine organisms. Based on the results of this paper, the polyglycerol-based emulsifiers and co-emulsifiers have proven suitable and recommended for use in high-performance environmentally friendly sun protection formulations.

Conflict of Interest Statement.

NONE.

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