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"Formulation Design for Clear Sunscreens"

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1. Introduction

Nowadays, sunscreens are an essential product to apply on the skin for consumers across the globe. Beyond the protection against sunlight, new types of sunscreen preparation and aesthetically pleasant format draw attention from consumers. Moreover, with the booming of clean beauty, the idea of "transparent" ramps up [1-2]. Conventional sunscreens containing either organic UV absorbers or inorganic particulates are opaque in appearance and leave consumers an impression of oily and heavy, sometimes with a whiting effect. Hence, it is of great challenge and high interest to formulate transparent sunscreens.

Biopolymers and synthetic polymers can form hydrogels loaded with high level (over 10 wt%) of hydrophilic UV filters, i.e. Disodium phenyl dibenzimidazole tetrasulfonat (DPDT) and Phenylbenzimidazole sulfonic acid (PBSA). The hydrogels structured by polymers can tolerate high levels of electrolyte strength and maintain desirable viscosity for application. The synergy between natural and synthetic polymers entitles to a robust hydrogel system for different combinations of hydrophilic UV filters. On the other hand, the inherently biodegradable oil thickener can offer various viscosity profiles for organic UV filter-based systems, from transparent gels to clear sticks, depending on the use level of the oil thickener.

Clear sunscreens can be achieved using powerful polymers such as natural (e.g. diutan gum) and synthetic (e.g. polyacrylates and polyurethane) ones. The UV protection performance of clear sunscreens was evaluated using *in vitro* SPF analysis method. Stability profiles were monitored over time and at elevated temperatures. The clear sunscreens formulated all show a potent UV protection performance. This work can serve as guidance on effectively formulating clear sunscreens with optimized stabilizers.

2. Materials and Methods

Materials

Polymer: Sphingomonas Ferment Extract (DG), Carbomer (U30) was used as supplied. Polyurethane-79 (PU-79) was used as supplier or together with Caprylic/Capric Triglyceride (CCT).

UV filters: Disodium phenyl dibenzimidazole tetrasulfonat (DPDT), Phenylbenzimidazole sulfonic acid (PBSA), Octocrylene (OCR), Ethylhexyl Salicylate (EHS), Diethylamino Hydroxybenzoyl Hexyl Benzoate (DHHB), Bis-ethylhexyloxyphenol Methoxyphenyl Triazine (BEMT), Ethylhexyl Triazone (EHT), Ethylhexyl Methoxycinnamate (EHMC), Homosalate (HMS), Butyl Methoxydibenzoylmethane (BMDBM). All organic UV filters were used as supplied.

Other ingredients: Caprylic/Capric Triglyceride (CCT), Diisopropyl Sebacate (DIS), Cocoyl Adipic Acid/Trimethylolpropane Copolymer (CATC), Neopentyl Glycol Diethylhexanoate (NGDO), Polyglyceryl-3 Laurate (TGL), Polyglyceryl-2 Diisostearate, Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG), Glycerin, Propanediol, 1,2-Hexanediol, Hydroxyacetophenone, Disodium EDTA, Sodium Gluconate, Aminomethyl Propanol (AMP), Sodium Hydroxide, Sodium Hyaluronate, and Dimethylmethoxy Chromanyl Palmitate were used as supplied.

Methods

Hydrogel preparation: 1. PART A: Under stirring, disperse carbomer (U30) into water. Keep mixing to hydrate. Add Sphingomonas Ferment Extract, mix until fully hydrated. Heat to 60-65 °C. 2. PART B: Under stirring and heating (60-65 °C), dissolve Aminomethyl Propanol into water. Add the UV-filters. Mix until the UV-filters are completely dissolved. Slowly and with continuous mixing add PART B to PART A. Stop heating. 3. Cool down to about 45 °C. 4. Under continuous mixing, add PART C ingredients one at a time to the batch. Mix well. 5. If necessary, adjust the pH using aminomethyl propanol to pH (7.5-7.8).

Table 1. Formulation table of hydrogel.

Phase	Ingredient Name	Weight %
A	Deionized Water	35.10
	Carbomer	0.30
	Sphingomonas Ferment Extract	0.35
B	Disodium Phenyl Dibenzimidazole Tetrasulfonate	8.00
	Phenylbenzimidazole Sulfonic Acid	4.00
	Deionized Water	39.00
	Aminomethyl Propanol (and) Water (Aqua)	3.50
C	Phenylpropanol (and) 1,2-Hexanediol	1.00
	Sodium hyaluronate	1.50
	Propanediol	2.00
	Glycerin	3.00
	Glycerin, Water (Aqua), Hydrolyzed Pea Protein, Glucose, Sodium Chloride, Sodium Succinate	2.00
	Polyglyceryl-3 Laurate	0.25

Structured oil preparation:

Oil gel: 1. Add ingredients into a suitable beaker one at a time. 2. Heat to 90 °C and mix until fully dissolved. 3. Fill it into containers while hot.

Table 2. Formulation table of oil gel.

Ingredient name	1 Weight %	2 Weight %	3 Weight %	4 Weight %
Caprylic/Capric Triglyceride (and) Polyurethane-79	3.00	3.00	3.00	3.00
Butyl Methoxydibenzoylmethane	3.00	0.00	3.00	3.00

Diethylamino Hydroxybenzoyl Hexyl Benzoate	0.00	4.00	5.00	5.00
Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	0.00	3.00	3.00	3.00
Ethylhexyl Triazone	0.00	3.00	5.00	5.00
Ethylhexyl MethoxyCinnamate	7.50	7.50	0.00	0.00
Ethylhexyl Salicylate	5.00	5.00	0.00	5.00
Homosalate	10.00	5.00	0.00	7.50
Octocrylene	10.00	6.00	0.00	6.00
Neopentyl Glycol Diethylhexanoate	20.00	20.00	20.00	20.00
Cocoyl Adipic Acid/Trimethylolpropane Copolymer	10.00	10.00	10.00	10.00
Diisopropyl Sebacate	31.50	33.50	51.00	32.50

Oil stick: 1. Heat phase A to 95-110 °C with constant stirring. Cool down to 80-85 °C. 2. Heat phase B to 80-85 °C with constant stirring. Add phase B to phase A. Mix well. Cool down to approximately 60 °C with constant stirring. 3. Add phase C with constant stirring. Fill the packaging containers.

Table 3. Formulation table of the sunscreen stick.

Phase	Ingredient Name	Weight %
A	Caprylic/Capric Triglyceride	47.25
	Neopentyl Glycol Diethylhexanoate	15.00
	Diisopropyl Sebacate	8.00
	Polyurethane-79	9.00
	Silica Dimethyl Silicate	1.00
B	Theobroma Grandiflorum Seed Butter	1.00
	Octocrylene	6.00
	Ethylhexyl Salicylate	4.00
	Diethylamino Hydroxybenzoyl Hexyl Benzoate	3.50
	Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine	2.00
	Ethylhexyl Triazone	2.00
	Polyglyceryl-2 Diisostearate	1.00
	Dimethylmethoxy Chromanyl Palmitate	0.10
C	Fragrance	0.15

Equipment
Hot plates with stirring function were used to blend the different phases. pH meter was used to determine the pH of the hydrogel. Rotational viscometer (Brookfield) was used to measure the viscosity of the formulations prepared. Helipath T-bar spindle was used for oil gels at 10 rpm.

Stability measurement
Sunscreen samples were subjected to stability evaluation at room temperature (RT), elevated temperature (50 °C) for 1 month, 45 °C for 3 months, and 5 freeze thaw (F/T) cycles at -18 °C for 24 hr and 25 °C for 24 hours. Visual inspection was used to assess the apparent stability of the samples.

In vitro SPF/UVAPF analysis

In vitro SPF and UVAPF values of optimized sunscreen samples were determined by UV-2000S (Labsphere). A 0.0325 ± 0.0005 g portion of sample was applied on a moulded Poly(methyl methacrylate) (PMMA) plate using an automatic robot arm and transmission of light was measured before and after solar simulation following ISO 24443 method. Each sample was repeated at least four times.

In vivo SPF test
In vivo SPF analysis was conducted on 3 volunteers following ISO 24444 method.

3. Results

The sunscreen hydrogel of **Table 1** was successfully prepared with a slightly yellowish appearance (**Figure 1**). The viscosity ranges from 3,000 to 4,500 mPa.s (Spindle #4 at 20 rpm). pH of the hydrogel was about 7.3 to 7.8 overs storage. The sample was stable up to 3 months at RT and 45 °*C,* 1 month at 50 °C*,* and passed 5 F/T cycles. The *in vivo* SPF test showed that this hydrogel sunscreen has a SPF of 27 based on 3 volunteers.

Figure 1. Face & body hydrogel SPF 25.

The clear sunscreen oil gels of **Table 2** were prepared with 3% PU-79 (with CCT) (see **Figure 2**). The viscosity ranges from 10,000 to 16,000 mPa.s (tested with spindle 94 at 10 rpm). All gels showed excellent clairty (NTU <10). The in vitro SPF/UVAPF test results reveal that the UV performance of the thickened sungel is good (see **Table 4**).

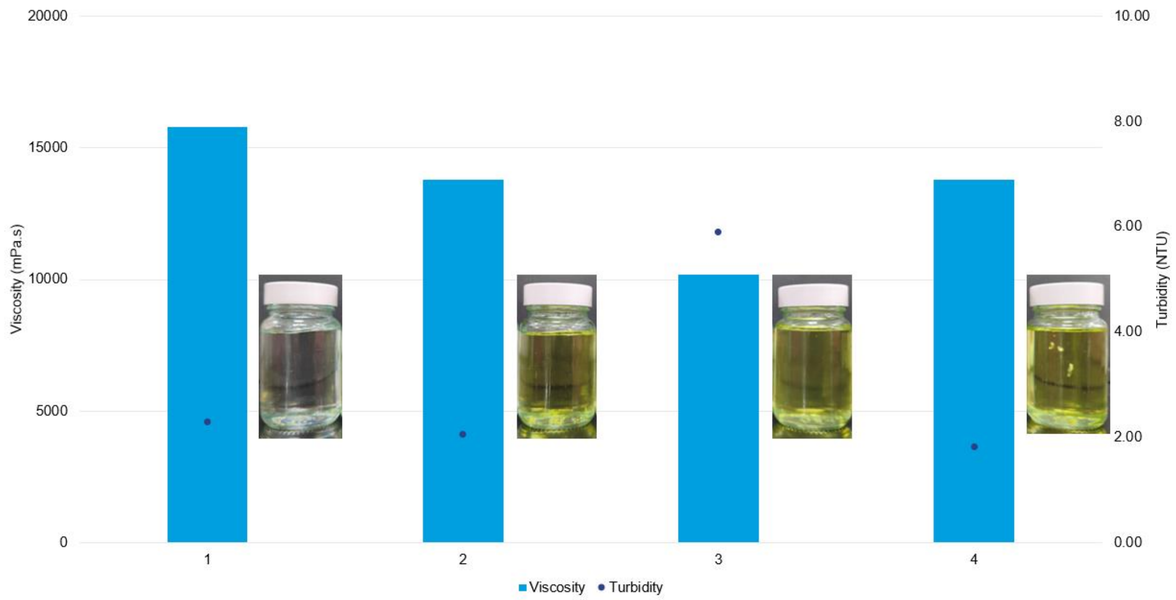

Figure 2. Viscosity and turbidity of sun gels prepared with organic UV absorbers, thickened by PU-79.

Table 4. *In vitro* SPF/UVAPF test results of PU-79 thickened sunscreen oil gels.

Sample	*In vitro* SPF	*In vitro* UVAPF	Lambda critical (nm)
1	30.19±3.88	7.97±0.24	373.60
2	29.25±4.41	9.90±0.36	369.85
3	30.32±4.16	22.70±2.41	376.00
4	34.03±5.88	13.93±0.22	376.90

The sunscreen stick of **Table 3** was successfully prepared with PU-79 at 9% (see **Figure 3**). The stability of this sunscreen stick passed the tests.

Figure 3. Sunscreen stick thickened by PU-79.

4. Discussion

Sunscreen hydrogels can be prepared using hydrophilic organic UV absorbers. These hydrophilic organic UV filters are electrolytes and are sensitive to pH environment [3-5]. They pose formulation challenges such as ionic strength and high pH requirement, which makes it difficult for hydrophilic stabilizers. In this study, U30 and DG were selected based on their electrolyte tolerance level and working pH. U30 can work well as a relatively high pH and exhibit a certain degree of electrolyte tolerance. On the other hand, DG showed synergy with electrolytes which boosts the viscosity and stabilization. An advantage of hydrogel sunscreen is its refreshing sensory, there is no touch of oily or greasy feel with such a hydrophilic base. When tested *in vivo*, it also provides a good level of protection against UV.

Clear sunscreen gels can be achieved using PU-79 with organic UV filters. PU-79 displayed high efficiency in building up the viscosity of purely oil-based systems. Meanwhile, it also improves the sensory with a powdery and soft feel. A noticeable merit of an oil-based system is the solubilization and stability of crystalline organic UV absorbers [6-7]. The high amount of oil ensures a powerful solubilization for UV filter crystals and prevents them from re-crystallization in the formulation. With a low use level of PU-79, oils can be thickened effectively and thus the application of the sunscreen product is easier than a flowing liquid. Pumps and tubes can be ideal packaging types for such a sunscreen format, convenient to carry and use.

Clear sunscreen sticks can be formulated with a higher use level of PU-79 (9%). The stick format is convenient, ideal for carrying handbags or using them anywhere, as it's compact and mess-free. Sunscreen sticks are easy to apply and even allow precise and controlled product application and re-application. Moreover, it can be further modified to be a concealer or for other purposes.

5. Conclusion

Formulation strategies to formulate clear sunscreen are: 1) for a hydrogel system, hydrophilic stabilizers with electrolyte tolerance and wide working pH range, such as U30 and DG, are preferred to work together with hydrophilic organic UV filters; 2) for oil-based systems, an efficient oil thickener such as PU-79 can be used to thicken hydrophobic organic UV filters offering a wide range of viscosity, thus texture (from gel to stick).

Although the UV protection performance largely depends on the UV filter system, selected stabilizers can help improve the aesthetic and sensory of the clear sunscreens. Oil thickeners, i.e. PU-79, may even enhance the UV protection by creating a uniform layer of UV filters on the skin for better coverage and protection.

6. Acknowledgments

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7. Conflict of Interest Statement

NONE.

8. Reference

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