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“Formulation Strategies for Emulsifier-free High Performance High Pigment Loading Hybrid and Mineral-based Oil-in-Water Sunscreens”

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1. Introduction

With growing attention to skin sensitivity and environmental impact, the demand for using inorganic UV particulates is increasing because of their safety and broad-spectrum protection [1]. For hybrid UV filter systems, synergies can be found between organic UV absorbers and mineral particulates, whereas claims such as natural sunscreens or hypoallergenic-friendly can be achieved will all-mineral UV filter systems [2]. Moreover, the trend towards easy-to-use and light skin feel urges the evolution of conventional heavy feel W/O mineral sunscreens to a fresh, easy to apply, and high-performance O/W preparations. Therefore, it is of great interest to challenge the potential of polymers to achieve new types of sunscreens containing inorganic UV filters with minimal ingredients yet high performance.

In this study, biopolymers and polyelectrolytes were tested as stabilizers for inorganic and organic UV filter systems. The pigment loading levels were investigated. Physicochemical and microscopic analysis was performed to understand the properties of the emulsifier-free emulsions. Stability tests were conducted to evaluate the robustness. Formulations were subject to in vitro SPF/UVAPF measurements to assess the UV protection performance.

The combination of biopolymers and polyelectrolytes successfully stabilized inorganic UV filters up to 30%. The network built by the polymers provides sufficient suspension power, and the hydrophobic interaction between polyelectrolytes and oil components enhances stability and ensures a stable pH environment with the presence of ZnO.

Emulsifier-free hybrid and all mineral sunscreens can be formulated with polymers, in line with consumer’s escalating expectations for a safer, natural, and high performing product. This study may entail the exploration of innovative formats of formulations for high pigment loading, freeing from the constraint of emulsifiers.

2. Materials and Methods

Materials

Stabilizers: Sphingomonas Ferment Extract (DG) and Caesalpinia Spinosa Gum (TG) were used as supply. Cellulose Gum was used as a mixture of Microcrystalline Cellulose, Sphingomonas Ferment Extract (PS). Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) was used as an aqueous solution with 30% active level. Acrylates/C10-30 Alkyl Acrylate Crosspolymer (PAA) was used as supplied.

UV filters: Zinc Oxide (ZnO), Zinc Oxide (and) Triethoxycaprylylsilane (ZX), Titanium Dioxide (and) Hydrated Silica (TW), Titanium Dioxide (and) Silica (and) Dimethicone (TX), Titanium Dioxide (and) Aluminium Hydroxide (and) Hydrated Silica (and) Hydrogen Dimethicone (TAS), Titanium Dioxide (and) Aluminum Hydroxide (and) Stearic Acid (TV). All inorganic UV particulates were used as supply. 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: Isostearyl Isostearate (1818), Isopropyl Isostearate (318), Diisopropyl Sebacate (DIS), Diisopropyl Adipate (DIA), C12-15 Alkane (CA), Phenoxyethanol (and) Ethylhexyl Glycerin (PEHG), Glycerin, Propanediol, 1,2-Hexanediol, Hydroxyacetophenone, Disodium EDTA, Sodium Gluconate, Aminomethyl Propanol (AMP), Sodium Hydroxide were used as supply. Polyhydroxylstearic Acid (PHSA) was used as a mixture with Neopentyl Glycol Diethylhexanoate (NGDO) as MS-1.

Methods

Preparation of hybrid sunscreens

The water phase (A) was first prepared using an overhead stirrer at 400 rpm until homogenous and heat to 65 °C. The oil phase (B) was weighed and mixed using a hot plate with stirring function, heated to 75 °C. TiO_2 powder (except TW) was added into oil phase and homogenized at 10,000 rpm for 3 min. Adding well mixed phase B into phase A and homogenized at 10,000 rpm for 3 min. Neutralize the phase (A+B) and cool down to room temperature.

Table 1. PAA-based emulsifier-free hybrid sunscreens

Hybrid	Batch No	TAS	TX	TW
Phase	Ingredient	wt%	wt%	wt%
A	Water	Q. S	Q. S	Q. S
	Glycerin	5.00	5.00	8.00
	Butylene Glycol	3.00	3.00	0.00
	Sodium Gluconate	0.20	0.05	0.10
	PEHG	0.50	0.50	0.60
	PAA	0.30	0.20	0.20
B	DHHB	4.00	3.00	4.00
	BEMT	3.00	0.00	3.00
	EHMC	7.50	7.50	7.50
	EHT	2.00	2.00	4.50
	EHS	4.50	4.50	4.50
	DIS	5.00	8.00	5.00

	C12-15 Alkane	5.00	0.00	0.00
	318	0.00	5.00	0.00
	MS-1	0.00	1.00	0.00
	TiO_2	5.00	5.00	2.00, 5.00
C	Neutralizer	to pH 6	to pH 6	to pH 6

Preparation of inorganic sunscreens

The water phase (A) was first prepared using an overhead stirrer at 400 rpm until homogenous. Neutralizer (B) was added to adjust the pH of the water phase (A). Inorganic particulates were added to the oil phase (C) and homogenized at 10,000 rpm for 3 min. The dispersion of pigments in oil phase (C) was added into the neutralized water phase under stirring. The mixture (A+B+C) was then homogenized at 10,000 rpm for 3 min.

Table 2. ASMC-based emulsifier-free inorganic sunscreen formulations with different biopolymers

Phase	Ingredient Name	ASMC	DG1	DG2	PS1	PS2	TG1	TG2
A	DI water	56.30	56.20	56.10	56.10	56.00	56.10	56.00
	Sodium Gluconate	0.10	0.10	0.10	0.10	0.10	0.10	0.10
	PEHG	0.60	0.60	0.60	0.60	0.60	0.60	0.60
	Glycerin	5.00	5.00	5.00	5.00	5.00	5.00	5.00
	DG	0.00	0.10	0.20	0.00	0.00	0.00	0.00
	PS	0.00	0.00	0.00	0.20	0.30	0.00	0.00
	TG	0.00	0.00	0.00	0.00	0.00	0.20	0.30
	ASMC	1.50	1.50	1.50	1.50	1.50	1.50	1.50
B	Sodium Hydroxide (20%)	to pH 7	to pH 7	to pH 7	to pH 7	to pH 7	to pH 7	to pH 7
C	1818	20.00	20.00	20.00	20.00	20.00	20.00	20.00
	MS1	1.50	1.50	1.50	1.50	1.50	1.50	1.50
	ZnO	10.00	10.00	10.00	10.00	10.00	10.00	10.00
	TV	5.00	5.00	5.00	5.00	5.00	5.00	5.00

Table 3. ASMC-based emulsifier-free inorganic sunscreen formulations with use level of oil

Phase	Ingredient Name	O1	O2	O3	O4
A	DI water	56.10	51.10	46.10	41.10
	Sodium Gluconate	0.10	0.10	0.10	0.10
	PEHG	0.60	0.60	0.60	0.60
	Glycerin	5.00	5.00	5.00	5.00
	DG	0.20	0.20	0.20	0.20
	ASMC	1.50	1.50	1.50	1.50
B	Sodium Hydroxide (20%)	to pH 7	to pH 7	to pH 7	to pH 7
C	1818	20.00	25.00	30.00	35.00
	MS-1	1.50	1.50	1.50	1.50
	ZnO	10.00	10.00	10.00	10.00

	TZ	5.00	5.00	5.00	5.00

Table 4. ASMC-based emulsifier-free inorganic sunscreen formulations with use level of inorganic UV particulates

Phase	Ingredient Name	P1	P2	P3	P4
A	DI water	54.60	51.60	47.10	39.60
	Sodium Gluconate	0.10	0.10	0.10	0.10
	PEHG	0.60	0.60	0.60	0.60
	Glycerin	5.00	5.00	5.00	5.00
	DG	0.20	0.20	0.20	0.20
	AMSC	1.50	1.50	1.50	1.50
B	Sodium Hydroxide (20%)	to pH 7	to pH 7	to pH 7	to pH 7
C	1818	20.00	20.00	20.00	20.00
	MS-1	1.50	3.00	3.00	3.00
	ZnO	10.00	12.00	15.00	20.00
	TV	5.00	6.00	7.50	10.00

Equipment
Overhead mixers and homogenizers were used to blend the different phases. pH and viscometer were used to measure the pH and viscosity values of the formulations prepared. Fineness gauge was used to assess the dispersion of particulates in formulations.

Microscope analysis
Optical microscopy was used to examine the microstructure of emulsion samples. A small amount of emulsion sample was placed on a microscope slide without dilution and covered by a cover glass slip. Samples were observed under transmitted light and polarizing light at 500 times magnification.

Stability measurement
Emulsion samples were subjected to stability evaluation at room temperature (RT), elevated temperature (50 °C) for 1 month, and centrifugation test at 3,000 rpm for 30 minutes. pH and viscosity were measured at 24 h RT, 1 month RT, and 1 month 50 °C. pH was measured by pH meter and viscosity by viscometer at 20 rpm at room temperature. Visual inspection was used to assess the apparent stability of emulsion samples.

In vitro SPF/UVAPF analysis
In vitro SPF and UVAPF values of optimized sunscreen samples were determined by UV-2000S (Labsphere). A 0.0300 ± 0.0005 g portion of sample was applied on a sandblasted Polymethyl 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.

3. Results

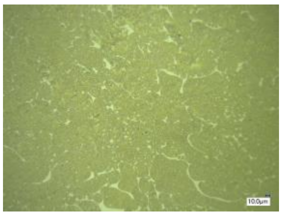
Emulsifier-free hybrid oil-in-water sunscreen emulsion

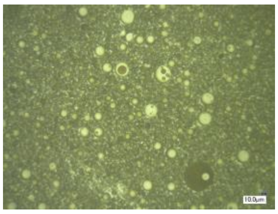
Stable oil-in-water emulsion containing 5% Titanium Dioxide can be formulated with PAA, with an oil loading up to 36%. The two types of hydrophobically coated Titanium Dioxide exhibited good stability over time. The emulsions stabilized by PAA showed viscosity ranging from 5,000-8,000 mPa·s. The water dispersible Titanium Dioxide was tested by two different process methods, adding before emulsification or after emulsification. Both procedures provided a stable emulsion with 0.2% PAA. The viscosity generated was slightly different, ranging from 3,000-6,000 mPa·s. Both 2% and 5% use levels of Titanium Dioxide can be well stabilized/suspended by 0.2% PAA in the system.

Emulsifier-free inorganic oil-in-water sunscreen emulsion

ASMC with biopolymers

Inorganic sunscreen emulsion prepared with AMSC alone was not stable over time and couldn't pass the centrifuge test. With the addition of biopolymers, the inorganic sunscreen emulsions can be well stabilized over time and passed centrifuge tests (microscope images see **Figure 1**). The emulsions prepared with PS showed the lowest viscosity (12,000-15,000 mPa·s), whereas TG offered the highest viscosity (25,000-45,000 mPa·s). However, texture and sensory wise, ASMC/TG provided the most appealing formulations.


DG1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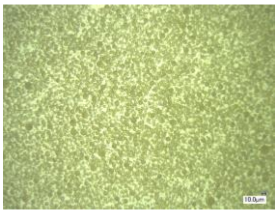
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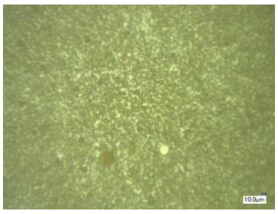
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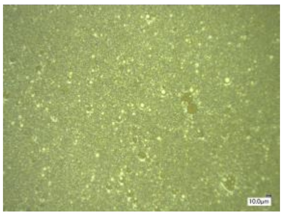

TG1

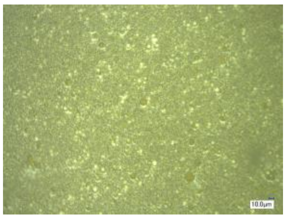
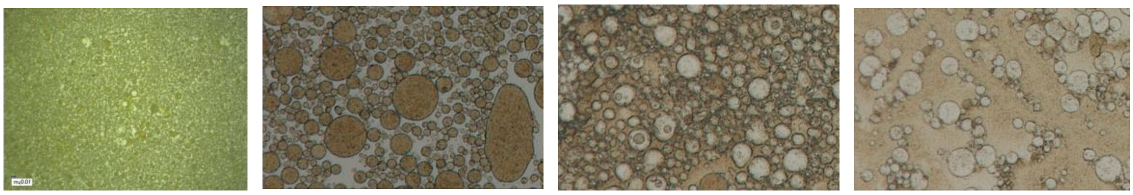

TG2

Figure 1. Microscope images of ASMC-based emulsifier-free inorganic sunscreen emulsion with different biopolymers.

Oil loading levels

Oil loading levels were tested at 20%, 25%, 30%, and 35% to disperse 15% of inorganic particulates (a combination of Zinc Oxide and Titanium Dioxide, at 10% and 5% respectively) (see **Figure 2**). 0.2% DG was used in combination with ASMC to stabilize the whole system. Based on the results, 20-30% of 1818 can work in the system. 35% of 1818 can't be stabilized with 15% of UV particulates over time (phase separation). The more 1818 in the system, the higher the internal phase, and thus higher the end-viscosity of the formula.

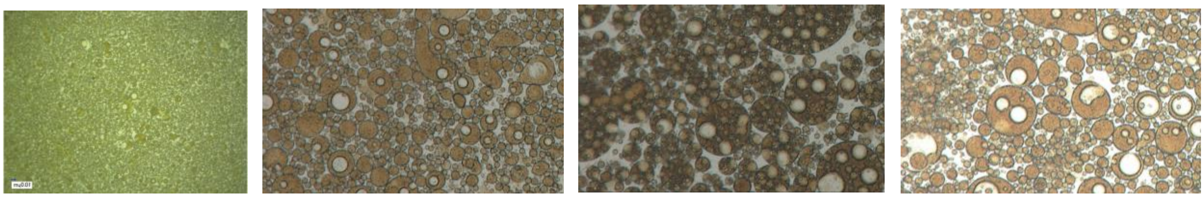


20% 1818 25% 1818 30% 1818 35% 1818

Figure 2. Microscope images of ASMC/DG-based inorganic sunscreen emulsion with different oil loading.

Pigment loading levels

The amount of inorganic UV particulates tested in ASMC/DG based emulsion was tested up to 30%, a considerably high loading of UF particulates in sunscreen. Four levels of ZnO/TiO_2 were tested in the same stabilizer system (15%, 18%, 22%, 30%). All the samples prepared were stable over time and passed centrifuge tests (microscope images see **Figure 3**). Viscosity ranges from 14,000 to 30,000 mPa·s, increasing amount of particulates leading to an increased viscosity.



15% 18% 22.5% 30%

Figure 3. Microscope images of ASMC/DG-based inorganic sunscreen emulsion with different loading of inorganic UV particulates.

4. Discussion

PAA is a powerful stabilizer for emulsifier-free oil-in-water emulsion, even with loading of Titanium Dioxide. PAA possesses both lipophilic and hydrophilic parts in its structure (see **Figure 4**). Upon neutralization, it swells in the water phase and form hydrogel structure with suspension power, and at the same time, interacting with hydrophobic components in the formulation to stabilize the interface. The yield value provided by PAA can help suspend TiO_2 particles in the formulation, regardless of the coating type of the particles.

For inorganic UV particulate-based emulsions, ASMC can work well with biopolymers to co-stabilize the whole system. ASMC is a hydrophobically modified polymer, showing great compatibility with different types of coated Titanium Dioxide (hydrated silica coated, silica coated, aluminum hydroxide coated, alumina coated) [3]. The stabilization power of ASMC mainly comes from the hydrophobic groups attached to the polymer backbone and the stretch of the backbone in the water phase (**Figure 5**). With the neutralization of the water phase, the backbone of ASMC will stretch out and thicken the water phase. When oil phase is added to the system, the hydrophobic associative groups can interact with the hydrophobic oil component, helping to stabilize the oil-water interface (**Figure 6**).

In general, it's very challenging to stabilize a high loading of pigment particles at 30% in an oil-in-water emulsion, not to mention, without emulsifiers. With the help of biopolymers, ASMC can tolerate high use level of inorganic UV particulates and keep the samples stable over time after preparation.

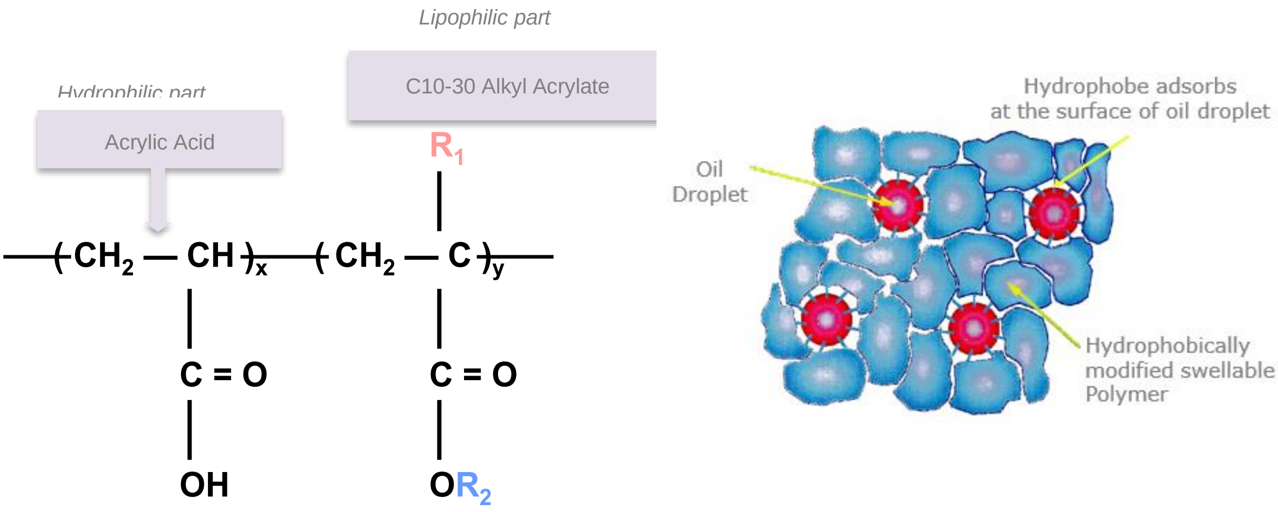


Figure 4. Structure of PAA polymer (left) and stabilization mechanism (right).

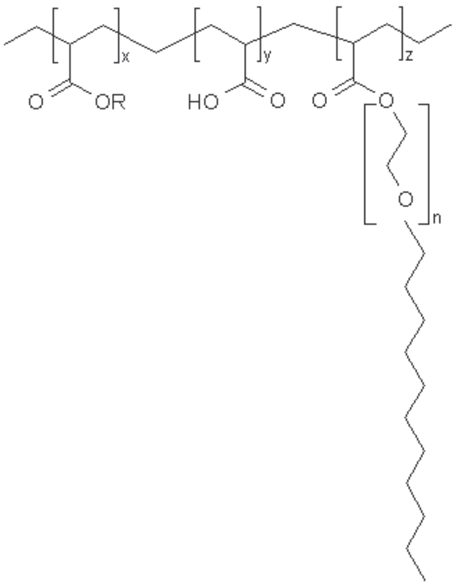


Figure 5. Structure of the hyper-HASE polymer where -x, y and z represent the moles of monomeric (methacrylic acid, acrylate and methacrylate esters) units in the backbone of the polymer and n is the moles of the ethylene oxide spacer connecting stearyl radical.

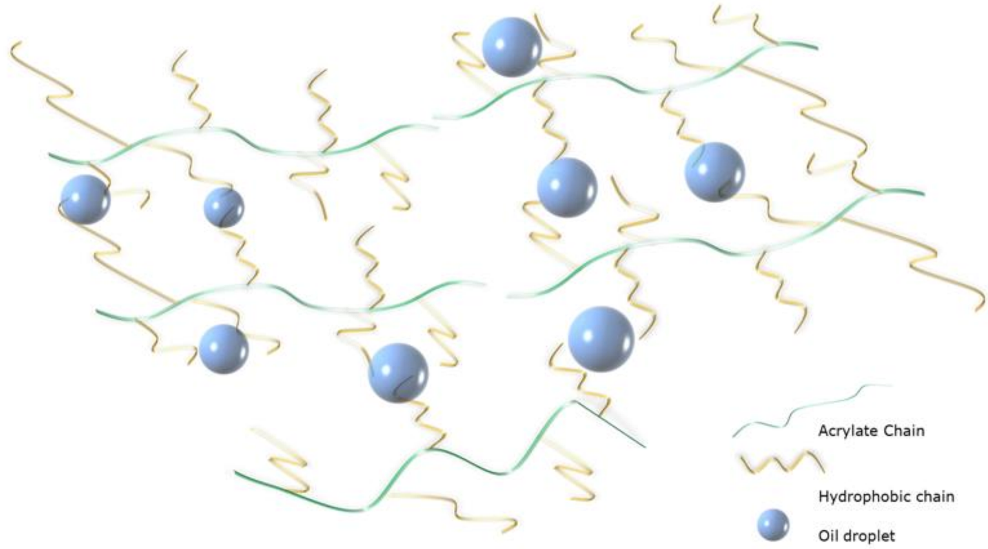


Figure 6. Illustration of working mechanism of Acrylates/Steareth-20 Methacrylate Copolymer (ASMC) for oil-in-water emulsion.

5. Conclusion

Emulsifier-free hybrid oil-in-water sunscreen emulsions can be prepared using PAA polymer for different types of Titanium Dioxide. Emulsifier-free inorganic oil-in-water sunscreen emulsions can be prepared using ASMC with biopolymers for various loading of inorganic UV particulates up to 30%.

6. Acknowledgments

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7. Conflict of Interest Statement

NONE.

8. Reference

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