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Lignin Oleate-Enhanced Tinted Mineral Sunscreens: Towards Inclusive Photoprotection for Skin of Colour

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Introduction

Currently, the cosmetic industry is still not inclusive in catering for a broad range of skin tones, particularly for consumers with melanin-rich skin. This is especially true in sun care (Geisler et al., 2021). An interest in more naturally-derived sun care formulations has grown, both due to chemophobia and fear of the impact of sun care formulas on human health and environmental safety (Wu et al., 2024). Lignin-based materials are steadily gaining interest in the cosmetic space due to their sustainable, multi-functional formulation benefits, along with their potential in enhancing the UV performance of sun care formulations (Espinoza-Acosta, Figueroa-Espinoza and Rosa-Alcaraz, 2022; Piccinino et al., 2022). This experiment explored lignin oleate's (LO) role as a functional active in sun care applications, its effect on the physical and organoleptic characteristics of a mineral sunscreen preparation with high naturality.

Materials and Methods

Table 1. Formulation

Phase	INCI	Trade Name	Supplier	A	B	C	D	E	F	G	H	I
				% (w/w)								
A	Aqua	---	---	68.90	58.90	63.45	53.45	58.90	48.90	48.45	43.45	38.45
A	Glycerin	---	---	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
A	Cellulose gum	natrathix™ bio cellulose	Ashland (US)	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
A	Disodium EDTA	Edeta BD	BASF (DE)	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
A	Phenoxyethanol (and) Ethylhexylglycerin	euxyl® PE 9010	Ashland (US)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
B1	Polyhydroxystearic Acid	Dispersun DSP-OL300	Innospec (US)	20.50	20.50	20.50	20.50	30.51	30.51	25.50	30.51	35.51
B1	Caprylic/Capric Triglycerides	Crodamol™ GTCC	Croda (GB)									
B1	C12-15 Alkyl Benzoate	Crodamol™ AB	Croda (GB)									
B2	Lignin Oleate (and) Oleic Acid	Roka Cirkle® Sotabosk	Roka Furadada (Spain)	---	---	---	---					
B2	Zinc Oxide (and) Stearic Acid	Solaveil MZP8	Croda (GB)	---	q.s. SPF ~10	---	q.s. SPF ~10	---	q.s. SPF ~10	Same as in D	Same as in D	Same as in D
B2	Iron Oxides (CI 77491, 77499, 77492) (and) Polycitronellol (and) Polyhydroxystearic Acid (and) Trihydroxystearin	CitroSperse™ Red, Black, and Yellow Iron Oxides	P2 Science (US)		---	q.s. ITA ~34º	q.s. ITA ~34º		---			
C	Sorbitan Stearate	Span 60	Croda (GB)	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
C	Polysorbate 60	Tween 60	Croda (GB)									
C	Cetearyl Alcohol	Crodacol™ 1618	Croda (GB)									

Manufacturing Method

Zinc Oxide was used in a concentration predicted to result in an SPF of ~10. The Iron Oxides were then combined to obtain tinted sunscreens matching an ITA of 30 – 35, which is considered a "dark" tone. As per Table 1, phases were prepared separately and combined via a hot-hot, high-shear process using a Silverson L5M (Silverson, UK) to obtain O/W systems. The final mixture was cooled while stirring with a propeller mixer.

Characterisation Methods

Oscillatory Amplitude Sweep

- Controlled strain
- Parallel plate geometry, 1.000 mm at 25 ± 0.20° C
- 1.000 Hz frequency with a strain range of 0.01000 – 100.0%
- 22 measurements recorded per run

Shear Rate Sweep

- Shear rate range of 0.001 - 100.00 s^{-1}
- Cone/plate geometry (2°, 0.100 mm) for formulations A - H
- parallel plate geometry (1.000 mm) for formulation I
- 25 ± 0.20° C

Colour Quantification

- L*a*b* values were measured for all tinted sunscreen samples
- Used to assess the impact of LO on the colour of sunscreens
- Used to assess colour change in stability testing
- L* and b* values were used to calculate ITA values using the following equation:
  ITA = [arctan(L*—50)/b*)] ·180/π

***In Vitro* SPF Testing**

- Performed by Croda
- Applied to sandblasted PMMA plates using HD Spreadmaster
- 9 readings were taken across each plate
- Measured between 250 - 450 nm

Thixotropy

- Three-step mechanical recovery test (5 s^{-1}, 100 s^{-1}, 5 s^{-1})
- Cone/plate geometry (2°, 0.100 mm)
- The mechanical recovery of samples was calculated by using the following equation:

% recovery = (average 10 viscosity readings of step 3 / average of 10 viscosity readings of step 1) · 100

Stability Testing

- Samples were stored in glass jars at 22 and 40 ± 1 °C for 6 weeks. Samples were then tested for their organoleptic and rheological properties compared to initial values.

Colour Quantification and *In Vitro* SPF Testing

LO showed substantial SPF boosting properties, while also reducing the ITA value of samples, i.e. darkening the shade. At 5%, it showed an SPF boost of almost 30% in Formulation G, along with a reduction in ITA from -22.85 in Formulation D to -45.19 in Formulation G. Higher percentages of LO (formulations H and I) only slightly reduced ITA values compared to formulation G and had a negative impact on SPF values.

Table 2: L and b* values obtained for Formulations B, C, D, F, G, H and I along with calculated ITA to compare to market benchmark; In vitro determination of SPF also included, along with photos of formulation swatches for visual comparison. Measurements recorded at Week 0. n=3.*

	Market Benchmark	C Fe$_2$O$_3$ Control	D Tinted SPF Control	G Tinted SPF + LO 5%	H Tinted SPF + LO 10%	I Tinted SPF + LO 15%	B ZnO Control	F ZnO + LO 10%
L*	41.93	41.06	44.76	38.52	36.36	34.23	87.55	55.78
b*	11.89	14.18	12.41	10.75	10.01	10.56	4.19	21.58
ITA (°)	−34.18	−32.25	−22.85	−45.19	−53.75	−56.22	83.68	15.00
SPF	---	1.8	15.9	20.5	18.0	10.9	9.5	13.4
Formulation swatch								

Results

Oscillatory Amplitude Sweep

Increasing LO resulted in increased stiffness (i.e. higher G*), probably due to the increasing oleic acid concentration. Phase angles were similar for all the samples; however, higher concentrations of LO appear to increase elastic behaviour. After 6-week stability, samples showed minor changes in behaviour, with LO-containing samples showing increased stiffness and elastic behavior. These shifts were more pronounced in the samples held at 40° C for 6 weeks.

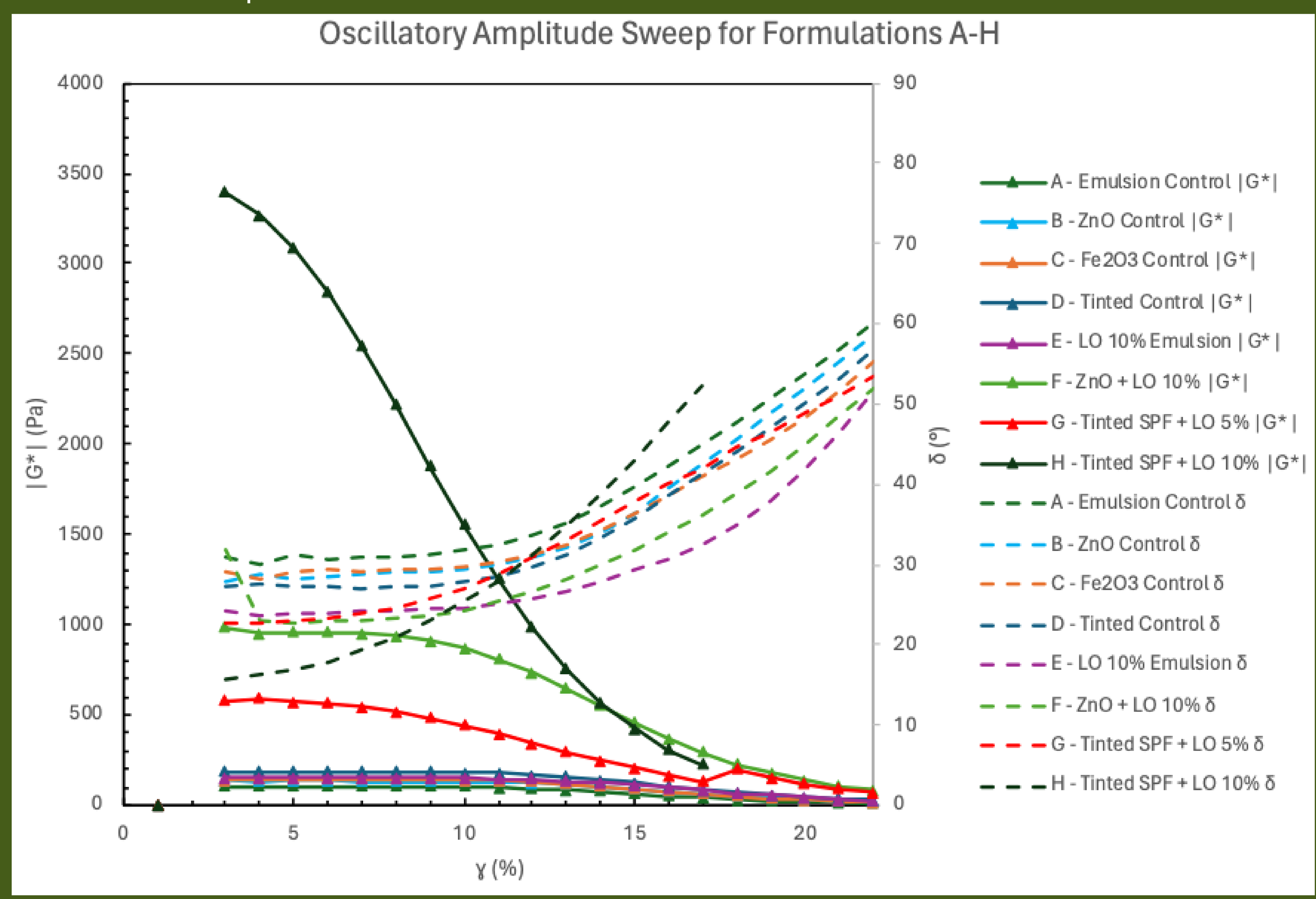

Figure 1. Graph displaying rheology data from oscillatory amplitude sweeps for Formulations A-H. n=3.

Viscosity

All formulations showed shear thinning behaviour, as expected, and increasing LO resulted in higher viscosity. Minimal change was observed after 6 weeks of stability testing at 22 ± 1°C, although the higher LO-containing formulations showed a slight increase in viscosity.

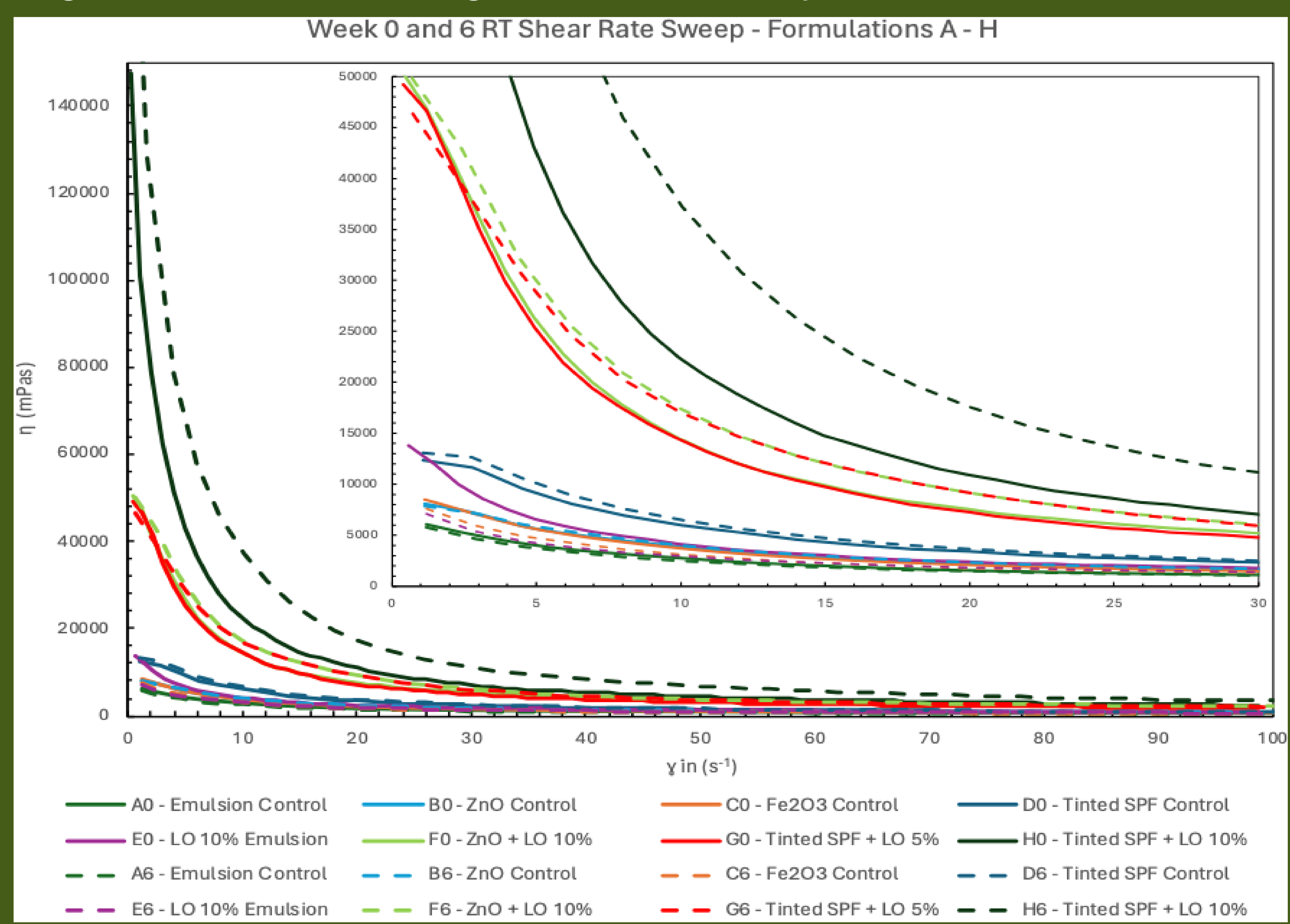

Figure 2: Graph displaying viscosity flow curves generated from shear rate sweeps at Week 0 and Week 6 at RT for Formulations A - H. Shear rate sweeps were performed at a range of 0.001 - 100.00 s^{-1}, with a focus of the 0.001 – 30.00 s^{-1} range provided for detailed view of shear-thinning comparison. n=3.

Mechanical Recovery

All formulations showed a high mechanical recovery. The addition of Zinc and Iron Oxides showed a trend of less recovery of structure, although all samples still demonstrated high degrees of recovery. Including LO resulted in a slight decrease in mechanical recovery properties.

Table 3: Mechanical recovery of emulsion structures for Formulations A, B, D, E, F, G, H, and I. n=3.

	A Emulsion Control	B ZnO Control	D Tinted SPF Control	E LO 10% Emulsion	F ZnO + LO 10%	G Tinted SPF + LO 5%	H Tinted SPF + LO 10%	I Tinted SPF + LO 15%
Recovery	92.37%	93.04%	88.91%	93.78%	85.22%	78.36%	74.68%	n/a

Discussion and Conclusions

Lignin oleate (LO) modified the rheological characteristics of the formulations showing a positive correlation between its concentration and emulsion structure. This may have been due to the increase in oleic acid, which was the carrier of LO. In the tinted formulations with ≥10% LO, phase inversion occurred, likely due to the high critical packing parameter of the oleic acid favouring the formation of W/O systems. This only occurred in the tinted formulations, where the oil phase volume was >50% of the overall formulation volume. 10% LO in the non-tinted emulsion did not demonstrate a phase inversion.

LO demonstrated high efficacy in boosting SPF in tandem with Zinc Oxide. With or without Iron Oxides, the SPF of the LO-containing formulations increased. 5% LO showed the best performance in the tinted formulations, where 10% and 15% showed subsequent drops in protection, likely due to emulsion phase inversion. LO also showed a substantial impact as a colourant, with only 5% LO dropping the ITA value of the tinted formulation down over 100%. Higher LO concentrations imparted less substantial deepening.

Overall, the experiment showed the rheology modifying, emulsifying, SPF boosting, and colourant benefits of the LO, although some of these benefits can be attributed to the oleic acid carrier of the LO. These attributes support its multi-functional formulation benefits. The ability of LO to reduce the ITA could be particularly useful in the development of formulations specific to individuals with skin of colour (SOC). LO can also be an upcycled biomaterial, helping drive sustainable innovation in inclusive sun care products (Espinoza-Acosta, Figueroa-Espinoza and Rosa-Alcaraz, 2022). Further work should assess LO's SPF and UVA-PF boosting capabilities alongside other established natural SPF boosters for creating high SPF mineral sunscreens with increased elegance for SOC. As a colourant, LO could also be used to reduce the concentration of Iron Oxides in tinted sunscreens and complexion products. Furthermore, LO's antioxidant properties could contribute to reducing UV-induced dyschromia in SOC (Piccinino et al., 2022).

References:

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