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Ethylcellulose oleogels as innovative sunscreen formulas: an exploration using rheology and texture analysis

Introduction

Oleogels present a potentially sustainable solution to developing waterless cosmetic products by reducing direct water consumption. They are also lightweight and may provide enhanced performance, potentially contributing to reducing carbon footprint in the cosmetic industry [1]. **Ethylcellulose (EC) oleogels offer versatile, water-conscious and innovative applications in cosmetics** [2], with enhanced sun protection factor (SPF) and compatibility with all kinds of UV filters in sunscreens[3].

The **aim of this study** was to evaluate the potential of EC oleogels as sunscreen formulations with a predicted SPF of 20-30, using emollients known to be good UV filter solvents.

Materials & Methods

A low-substitution EC was used (Aqualon™ EC-N200 PC, Ashland, US). The oils, surfactant and UV filters used in this study are presented in **Table 1**.

Rheological characterisation was performed with a HAAKE™ MARS™ iQ Air Modular rheometer with a parallel plate geometry with a 0.5 mm gap (Thermo Fisher Scientific, USA) at 20º C. Shear rate sweep (0.1 s^{-1}–100 s^{-1}) was used to measure viscosity. Oscillatory stress sweep (1–500 Pa, 1 Hz) was used to measure complex modulus (G*) and phase angle (δ). Yield stress was calculated according to Tamburic et al. [4]. Firmness, spreadability and stickiness were tested using a TA.XTplus Texture Analyser (Stable Micro Systems, UK), with a TTC Spreadability Rig and Heavy Duty Platform at 23 ± 1º C.

Manufacturing Method

The compositions of **EC (E and EM) oleogels**, **EC oleogels with SMS (EC/SMS)** and **sunscreen (S) oleogels** are detailed in **Table 1**. They were manufactured by heating all ingredients to 150º C and stirred (250 rpm) whilst cooling.

Table 1. Oleogel composition.

		% (w/w)													
INCI		E1	E2	E3	E4	EM1	EM2	EM3	EM4	MS1	MS2	MS3	MS4	S1	S2
Ethylcellulose (EC)		5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.00	5.00	5.00	5.00	5.00	5.00
C12-15 Alkyl Benzoate (AB)		95.0	-	-	-	47.5	47.5	31.67	29.0	45.50	45.50	30.30	27.67	26.50	24.83
Dicaprylyl Carbonate (DC)		-	95.0	-	-	47.5	-	31.67	29.0	45.50	-	30.30	27.67	26.50	24.83
Caprylic/Capric Triglycerides (CCT)		-	-	95.0	-	-	47.5	31.67	29.0	-	45.50	30.30	27.67	26.50	24.83
Dibutyl Adipate (DA)		-	-	-	95.0	-	-	-	8.0	-	-	-	8.00	8.00	8.00
Sorbitan Monostearate (SMS)										**4.00**	**4.00**	**4.00**	**4.00**	-	**4.00**
UV Filters	**Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine**													5.00	5.00
	Ethylhexyl Methoxycinnamate													5.00	5.00
	Butyl Methoxydibenzoylmethane													2.50	2.50

Results – Viscosity

- E1 and E3 were stable; E2 showed oil syneresis and E4 did not form an oleogel. **AB was selected as the base emollient** in this study for its high polarity, good UV filter solubilising properties [5] and ability to form stable oleogels.
- **Figure 1**: all EC oleogels were shear thinning and oleogel viscosity increased with more emollients added to AB.
- **Figure 2**: the viscosity of all EC/SMS oleogels was similar, regardless of the number of emollients used, suggesting that SMS crystalline network may have a greater effect than EC-solvent interactions in determining oleogel viscosity [6].
- **Figure 3**: UV filters altered the original viscosity of EC and EC/SMS oleogels. This is likely due to the complex structure of UV filters affecting the molecular packing at solvent level and the ability to interact with EC.

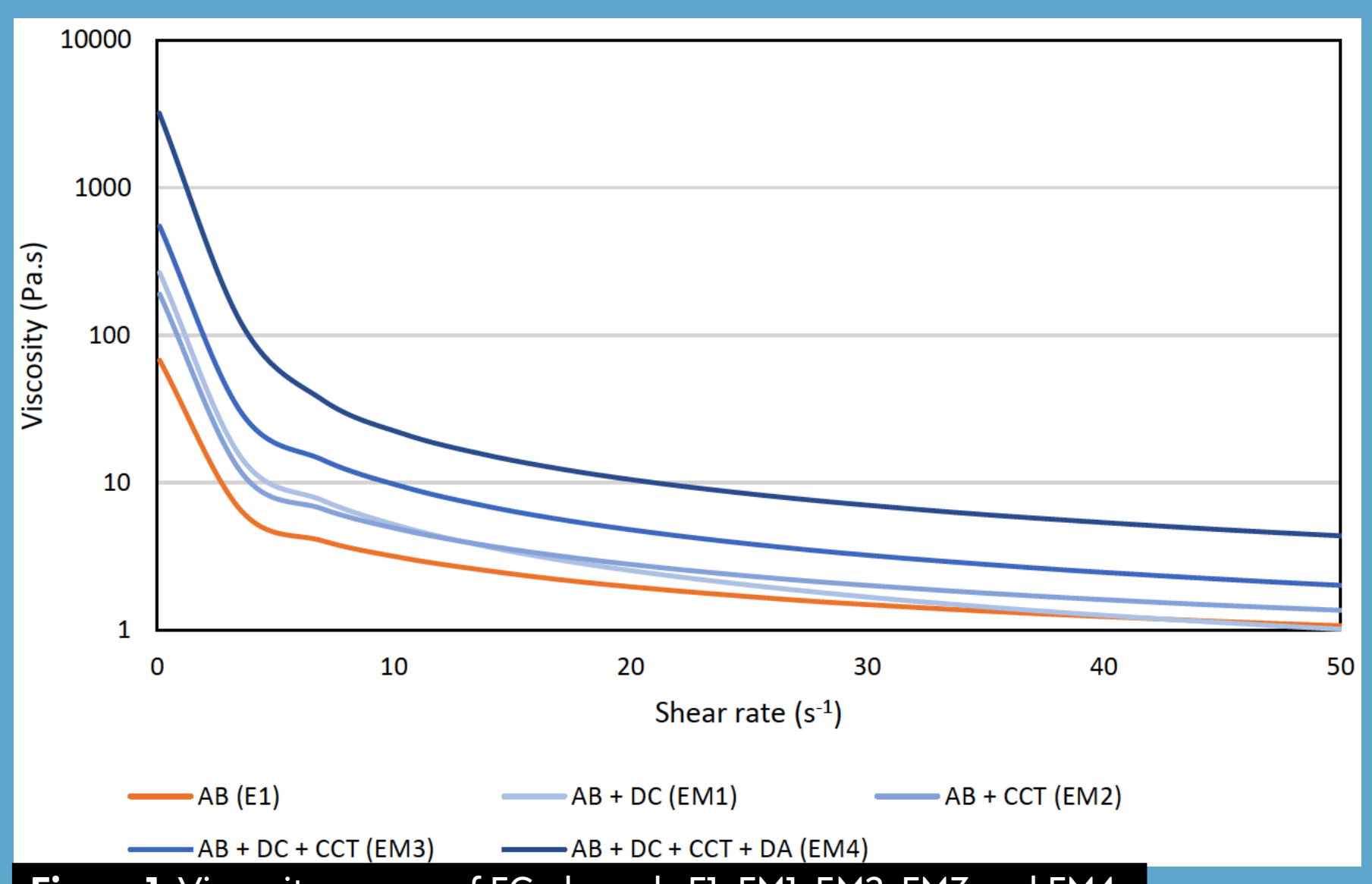

Figure 1. Viscosity curves of EC oleogels E1, EM1, EM2, EM3 and EM4.

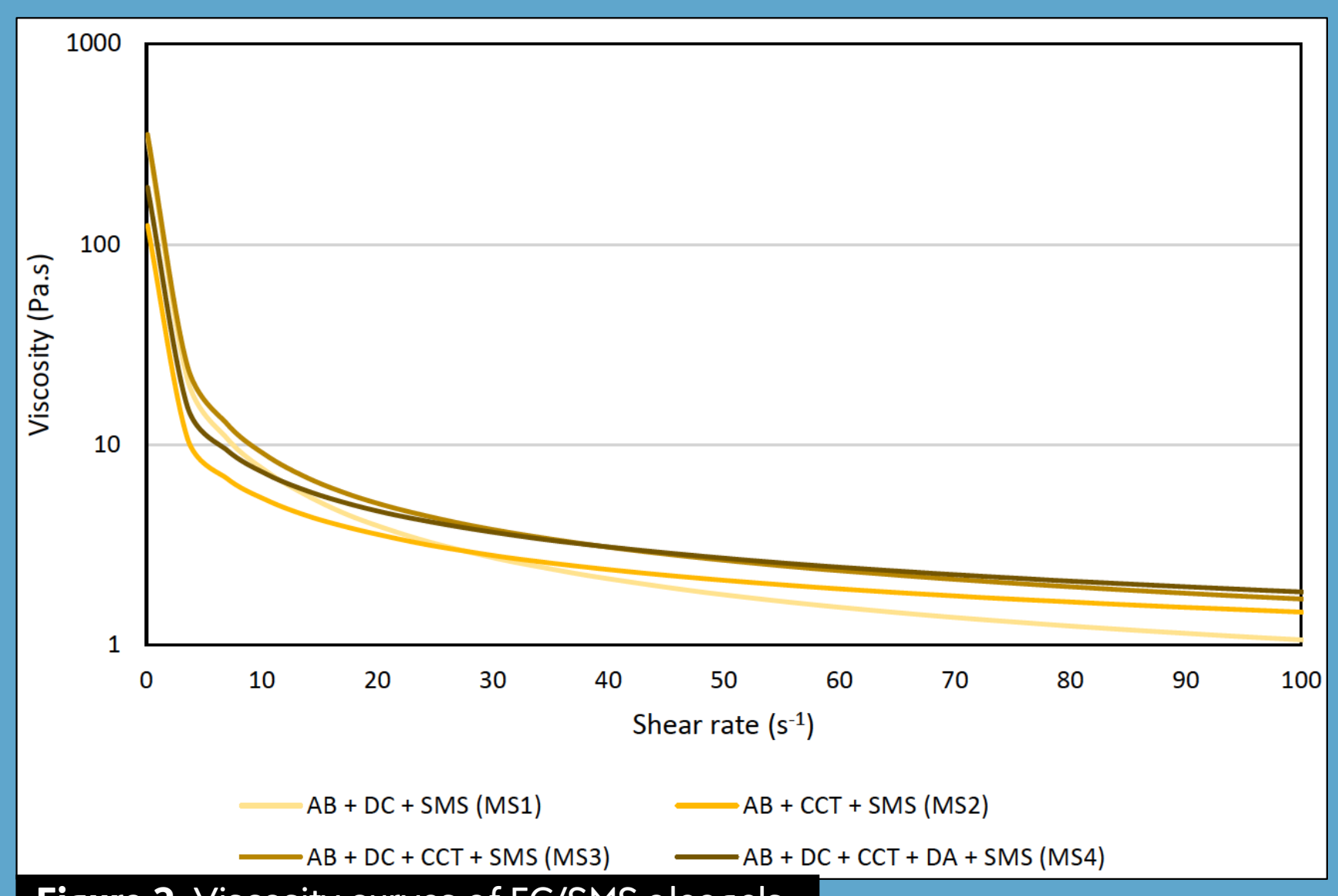

Figure 2. Viscosity curves of EC/SMS oleogels.

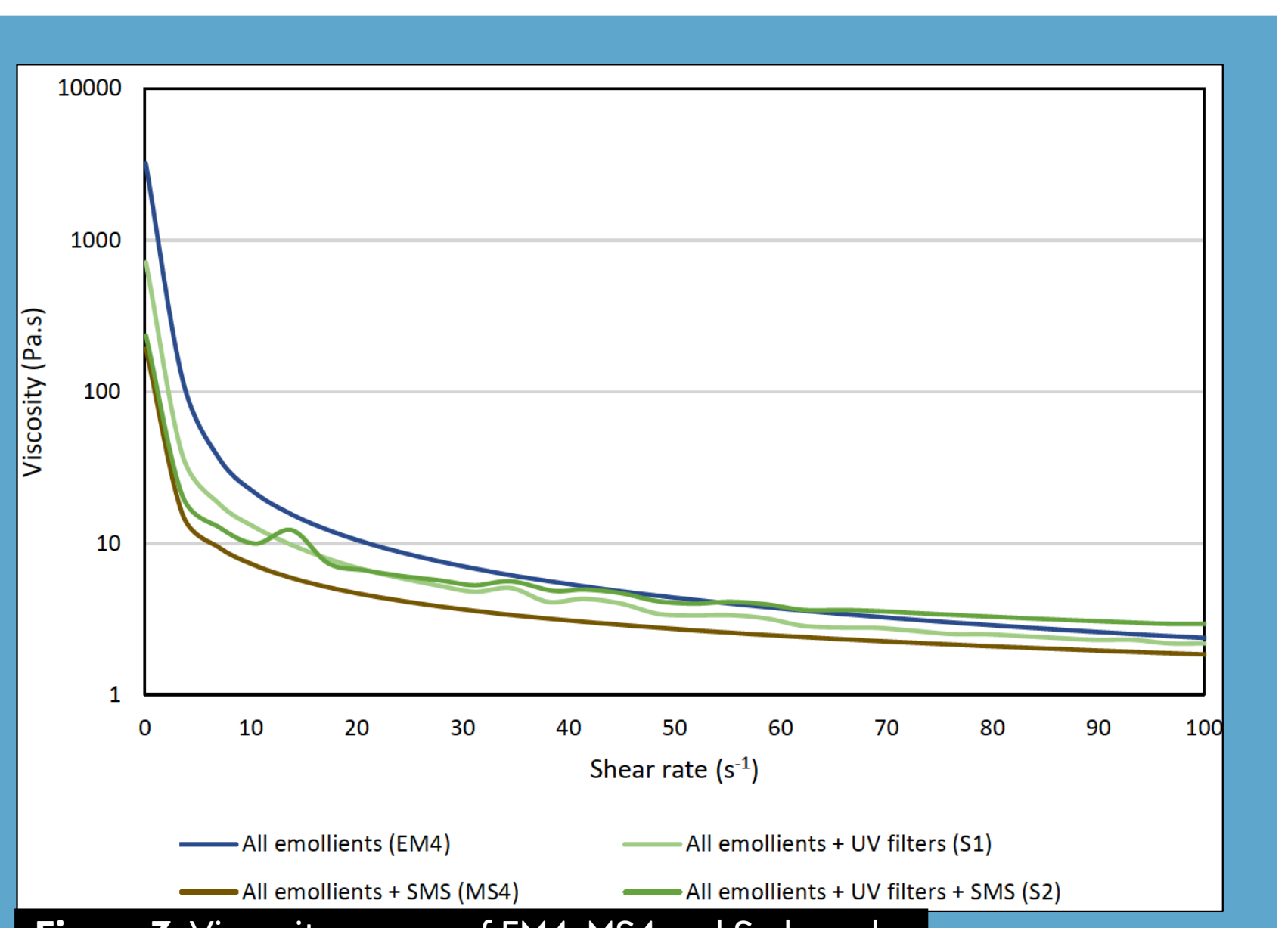

Figure 3. Viscosity curves of EM4, MS4 and S oleogels.

Results – Viscoelastic Properties

- **Figure 4**: the complex moduli and yield stress values (**Table 2**) of EC oleogels increased with increasing number of emollients. This is in line with the viscosity behaviours shown in Figure 1. However, no pattern was observed for the phase angle.
- **Figure 5**: although the complex moduli of EC/SMS oleogels varied, their phase angle was very similar, in line with the literature – SMS has previously shown to have a determining effect on the elasticity of EC/SMS oleogels [7].
- **Figure 6**: again, SMS caused MS4 and S2 to have similar complex moduli, both considerably lower than EM4 and S1, respectively. UV filters decreased the phase angle (higher elasticity) in the absence of SMS (EM4 vs S1), but in the presence of SMS, UV filters increased the phase angle (MS4 vs S2).
- **Table 2**: the yield stress values of EC/SMS oleogels were similar, again suggesting the important effect of SMS networks in the physical properties of EC oleogels [6]. The yield stress of S1 and S2 was higher than EM4 and MS4, respectively.

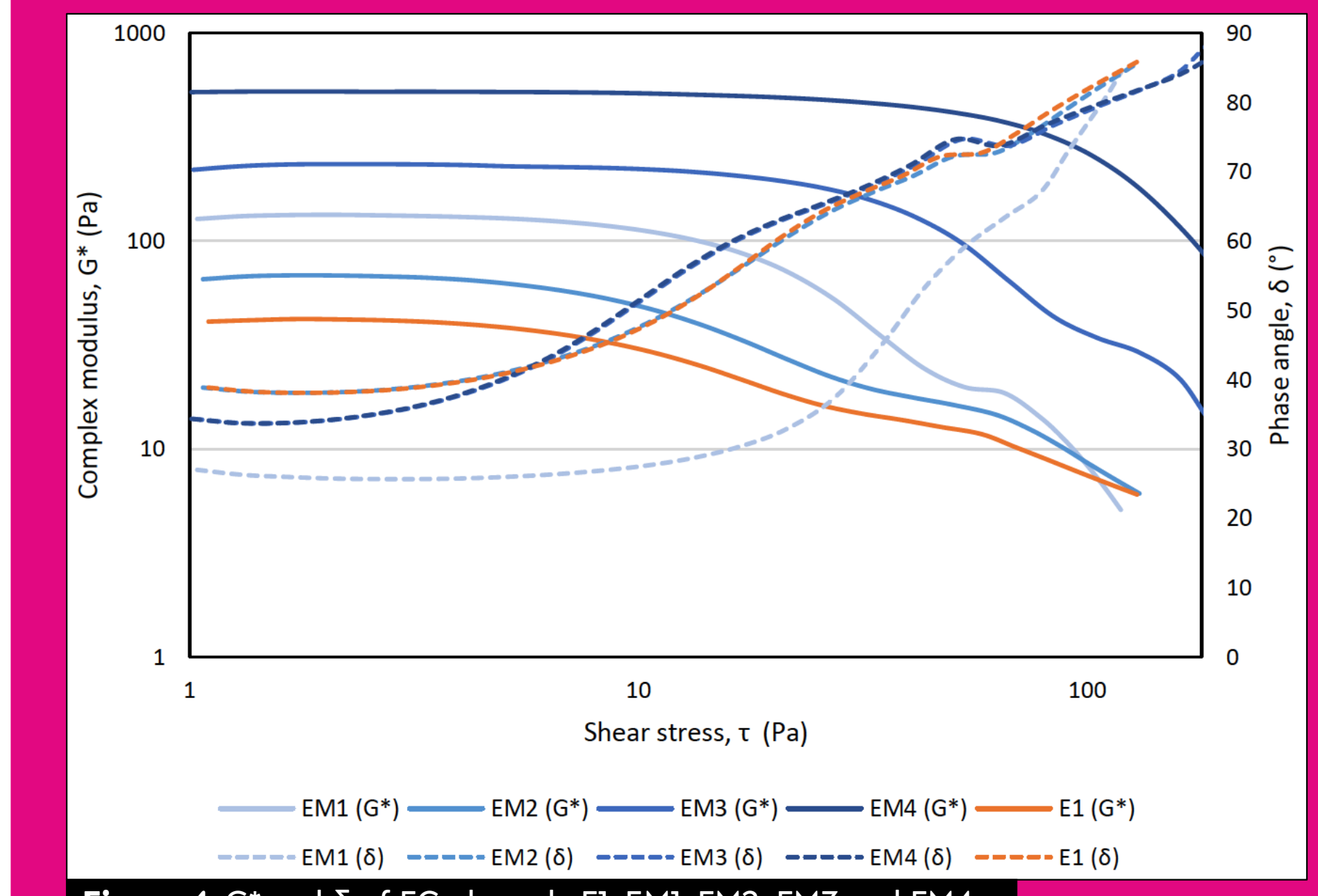

Figure 4. G* and δ of EC oleogels E1, EM1, EM2, EM3 and EM4.

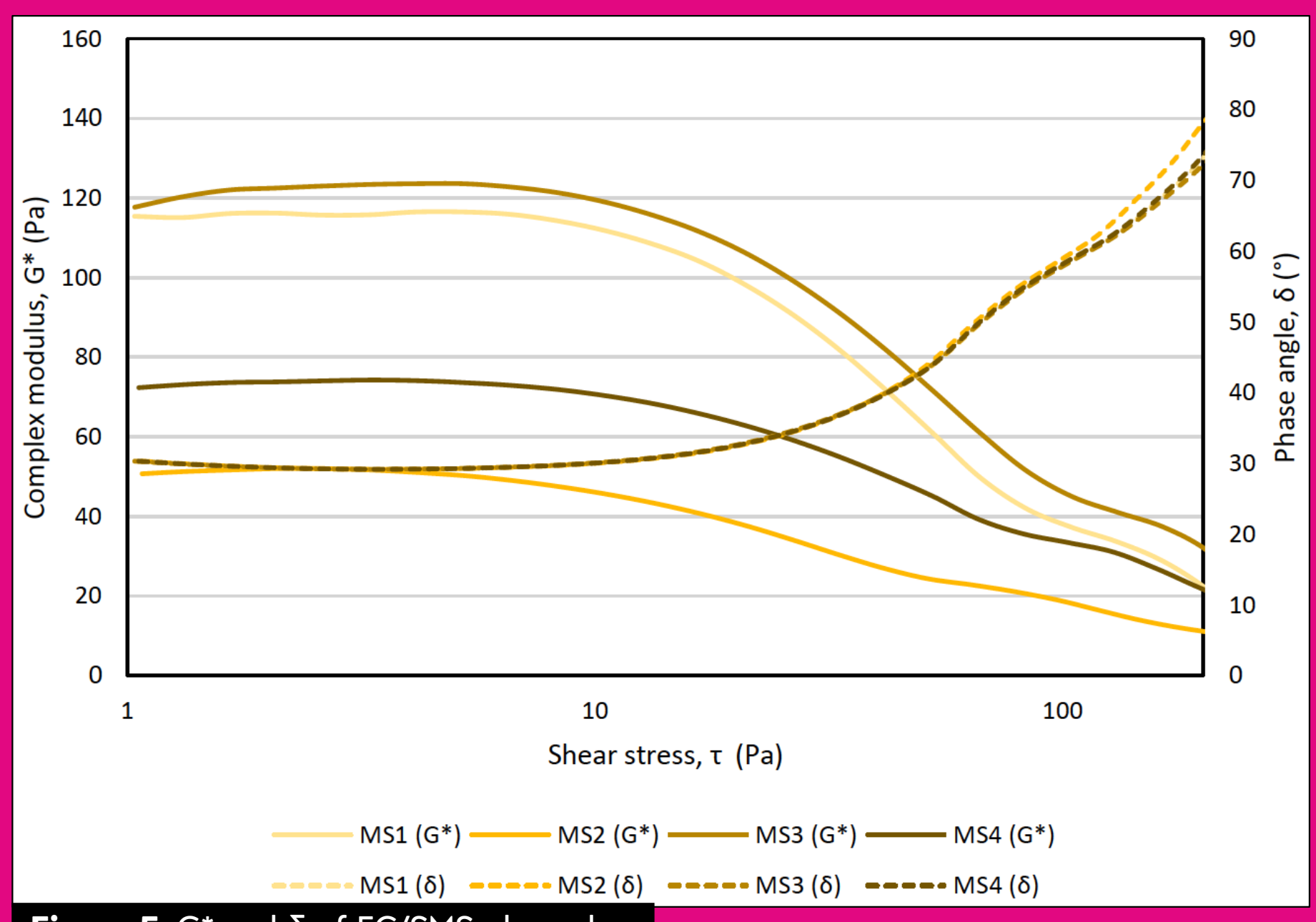

Figure 5. G* and δ of EC/SMS oleogels.

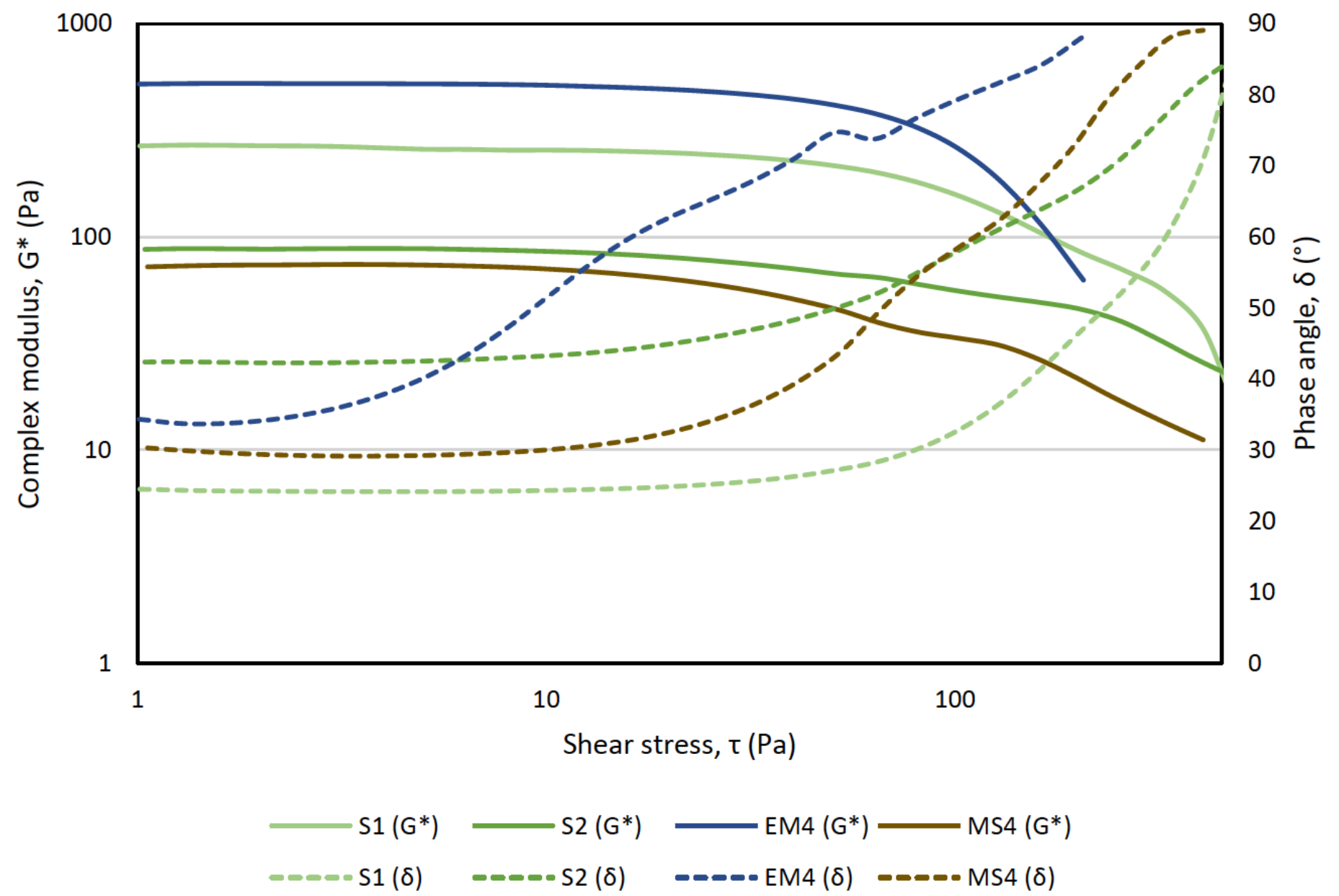

Figure 6. G* and δ of EM4, MS4 and S oleogels.

Table 2. Yield stresses of EC, EC/SMS and S oleogels.

Oleogels		Yield Stress (Pa)	Figure
EC oleogels	EM1	8.38	4
	EM2	6.32	4
	EM3	14.66	4
	EM4	28.72	4 & 6
EC/SMS oleogels	MS1	16.57	5
	MS2	10.76	5
	MS3	16.52	5
	MS4	15.06	5 & 6
S oleogels	S1	29.03	6
	S2	20.82	6

Results – Textural Analysis

- **Table 3**: all **oleogels showed similar firmness, spreadability** (inversely proportional to work of shear) **and stickiness**, except for S1. Both **S1 and S2 were firmer, more sticky and less spreadable** than EM4 and MS4, respectively, suggesting that UV filters affect the physical properties of EC oleogels independently of SMS. Although MS4 has shown lower viscosity (Figure 2) and lower complex modulus (Figure 5) than EM4, this pattern was not observed in textural analysis. Texture analysis has been correlated with sensory properties [8], therefore the perceived differences between different oleogels should be investigated in the future.

Table 3. Firmness (g), work of shear (g s), and stickiness (g) of EM4, MS4, S1 and S2 oleogels (mean ± standard deviation).

Oleogel	Firmness (g)	Work of Shear (g s)	Stickiness (g)
EM4	576.08 ± 42.98	498.27 ± 33.55	-577.98 ± 17.64
MS4	561.10 ± 27.39	410.90 ±37.45	-654.79 ± 21.98
S1	1221.91 ± 146.04	1173.98 ± 212.35	-804.19 ± 53.22
S2	654.30 ± 26.29	488.78 ± 11.68	-782.74 ± 19.66

Conclusion

Increasing number of emollients increased oleogel viscosity, yield stress and stiffness. This could be attributed to hydrogen bonding between functional groups of cosmetic oils and hydroxyl groups in EC. However, SMS crystalline networks appear to dominate over EC polymer networks. Higher yield stresses and higher elastic properties at low stresses of EC/SMS oleogels could explain their overall better stability. Overall, **EC oleogels have shown considerable potential as bases for sunscreen applications**.

References: [1] Aguiar JB, Martins AM, Almeida C, Ribeiro HM and Marto J (2022) 'Water sustainability: A waterless life cycle for cosmetic products. Sustain Prod Consum, 32:35-51. [2] Cosmetics Business (2019) Blue Gold: Water in Cosmetics. [3] Esposito CL, Kirilov P (2021) Preparation, Characterization and Evaluation of Organogel-Based Lipstick Formulations: Application in Cosmetics. Gels 7(3):97. [4] Tamburic S, Sisson H, Cunningham N, Stevic MC (2017) Rheological and Texture Analysis Methods for Quantifying Yield Value and Level of Thixotropy. SOFW Journal 143:24-30. [5] BASF (n.d.) BASF Emollients – Choosing the right Emollient. BASF Personal Care and Nutrition GmbH. [6] Murdan S, Gregoriadis G, Florence AT (1999). Novel sorbitan monostearate organogels. J Pharm Sci, 88(6):608-614. [7] Dey T, Kim DA, Marangoni AG (2011) Chapter 13: Ethylcellulose Oleogels, in: Marangoni AG and Garti N (ed.) Edible Oleogels, Structure and Health Implications. Urbana: AOCS Press. 295-311. [8] Calixto LS, Infante VHP, Maia Campos PMBG (2018) Design and Characterization of Topical Formulations: Correlations Between Instrumental and Sensorial Measurements. AAPS Pharm Sci Tech, 19:1512-1519.