

Waterless EC oleogels as innovative cold-cold emulsion bases

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INTRODUCTION

Ethylcellulose (EC) is an oleogelator compatible with various cosmetic emollients and surfactants [1]. EC oleogels have potential as cold-cold emulsification bases, reducing thermal energy consumption in manufacturing [2]. These bases could help reduce the carbon footprint of supply chains by removing the volume and weight of water; these bases could then be emulsified locally. **This project investigated the feasibility of EC oleogels as innovative emulsion bases for sustainable cold-cold emulsification.**

MATERIALS & METHODS

Materials & Formulation: Ethylcellulose (**EC**); Sorbitan Stearate (**SMS**); Polysorbate 60 (**P60**); Ricinus communis (Castor) oil (**CO**); Linum usitatissimum (Linseed) oil (**LO**); C12–15 Alkyl Benzoate (**AB**); and Caprylic/Capric Triglycerides (**CCT**). Materials combined as per Tables 1, 2 and 3 and the method in Figure 1. **Legend for Tables 2, 3 and 4:** hot-hot process; cold-cold process; unstable. **Rheological characterisation:** HAAKE MARS iQ Air rheometer (Thermo Fisher Scientific, UK); parallel plate geometry (0.500 mm gap; oleogels: $\varnothing$ 60 mm; emulsions: $\varnothing$ 35 mm); 20° C. Amplitude sweep (1–500 Pa; 1 Hz); and shear rate sweep (oleogels: 0.001–100 s⁻¹; emulsions: 0.1–200 s⁻¹). **Texture analysis (emulsions):** TA.XTPlus Texture Analyser (Stable Micro Systems, UK); TTC spreadability rig; triplicate measurements; 21° C.

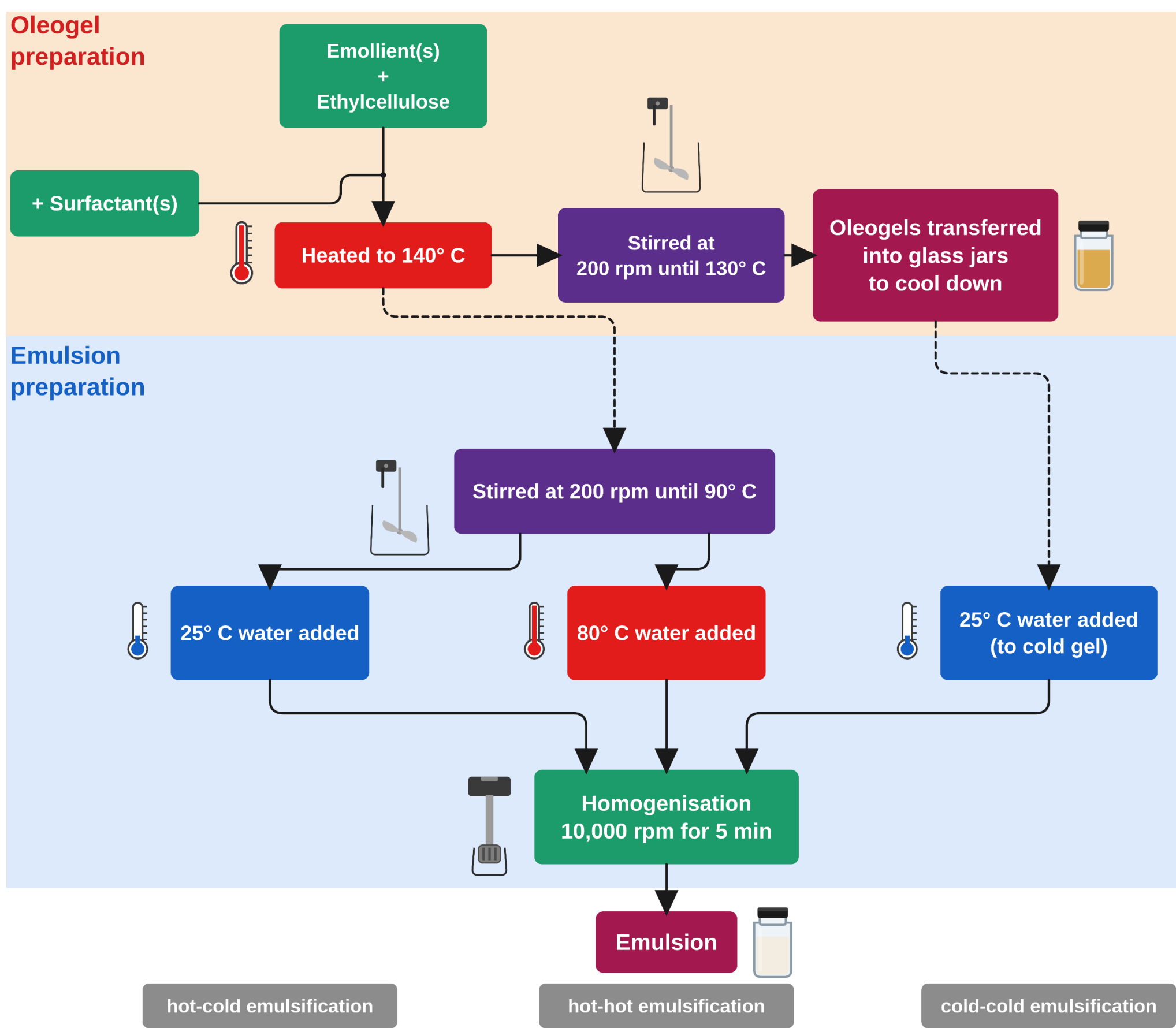


Figure 1: Preparation flow chart for EC oleogels and their respective emulsions.

Table 1: Composition of oleogels without surfactant, with SMS and with SMS+P60. Stable samples (1 month) in bold.

Oleogel	EC	CO	LO	AB	CCT	SMS	P60
% (w/w)							
O1	5.00	95.00	-	-	-	-	-
O2	5.00	-	95.00	-	-	-	-
O3	5.00	-	-	95.00	-	-	-
O4	5.00	-	-	-	95.00	-	-
M1	5.00	47.50	47.50	-	-	-	-
M4	5.00	-	-	47.50	47.50	-	-
M5	5.00	23.75	23.75	23.75	23.75	-	-
OS1	5.00	91.00	-	-	-	4.00	-
MS1	5.00	45.50	45.50	-	-	4.00	-
MS4	5.00	-	-	45.50	45.50	4.00	-
MS5	5.00	22.75	22.75	22.75	22.75	4.00	-
OSP1	5.00	91.00	-	-	-	2.00	2.00
MSP1	5.00	45.50	45.50	-	-	2.00	2.00
MSP4	5.00	-	-	45.50	45.50	2.00	2.00
MSP5	5.00	22.75	22.75	22.75	22.75	2.00	2.00

Table 2: Composition of CO oleogel emulsions.

	E1	E2	E3	E4
% (w/w)				
EC	3.75	-	3.75	3.75
SMS	1.50	1.50	3.00	-
P60	1.50	1.50	-	-
CO	68.25	72.00	68.25	71.25
Aqua	25.00	25.00	25.00	25.00

Table 3: Composition of oleogel emulsions with oleogels from Table 1.

	E1	ME1	ME4	ME5
% (w/w)				
Oleogel Phase	OSP1	75.00	-	-
	MSP1	-	75.00	-
	MSP4	-	-	75.00
	MSP5	-	-	-
	Aqua	25.00	25.00	25.00

RESULTS

Figure 2a: all oleogels were shear thinning. O1 was ~5 times more viscous than other EC oleogels, due to CO–EC hydrogen bonding [3]. **Figure 2b:** CO increased viscosity (M1 > M5 > M4). Only oleogels containing CO remained stable (O1, M1, M5): therefore, **CO is a key ingredient in obtaining stable EC oleogels.** **Figure 3a:** both complex modulus (G^*) and phase angle (δ) increased by adding SMS, due to a plasticising effect [4]. P60 reduced yield point and resulted in OSP1 having similar G^* to O1, but a δ similar to OS1; **this could lower mechanical energy during emulsification.** **Figure 3b:** all oleogels with SMS, P60 and CO (OS1, OSP1, MS1, MS5, MSP1, MSP5) were stable, whereas those without CO (M4, MS4, MSP4) were unstable. Oleogel viscosity was, again, dependent on CO concentration: OSP1 > MSP1 > MSP5.

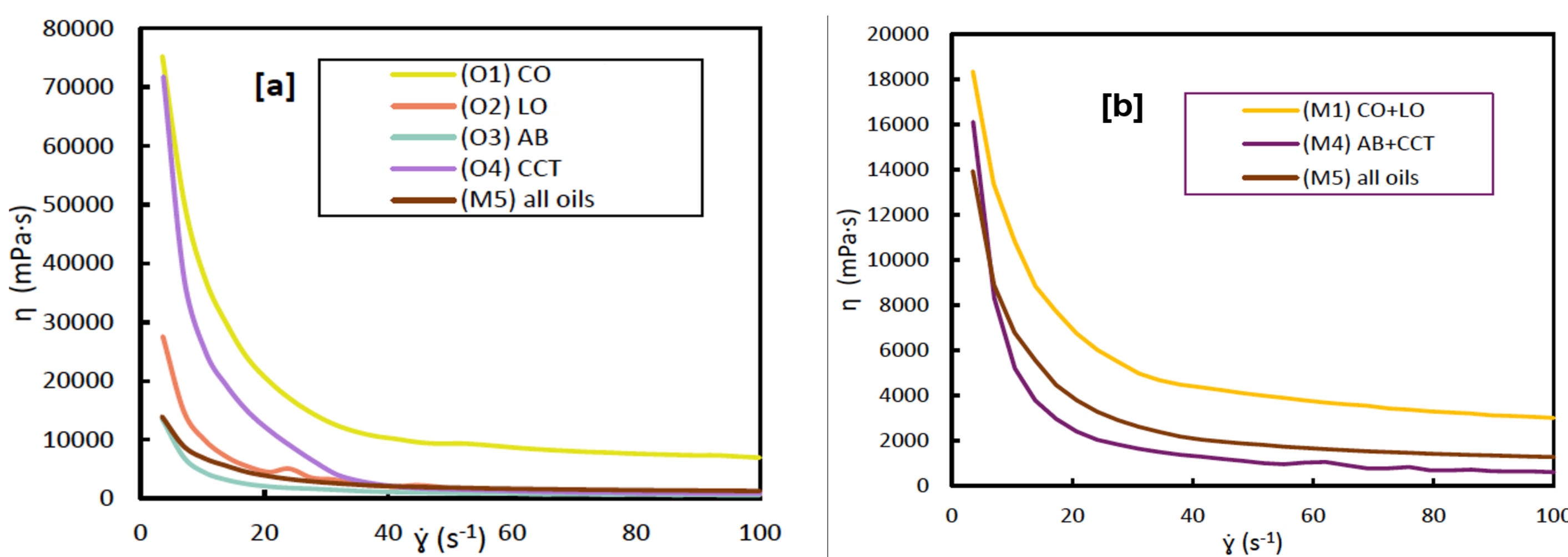


Figure 2: [a] Viscosity of EC oleogels with CO (O1), LO (O2), AB (O3), CCT (O4), and a mixture of all oils (M5). [b] Viscosity of EC oleogels made with oil mixtures CO+LO (M1), AB+CCT (M4), and CO+LO+AB+CCT (M5).

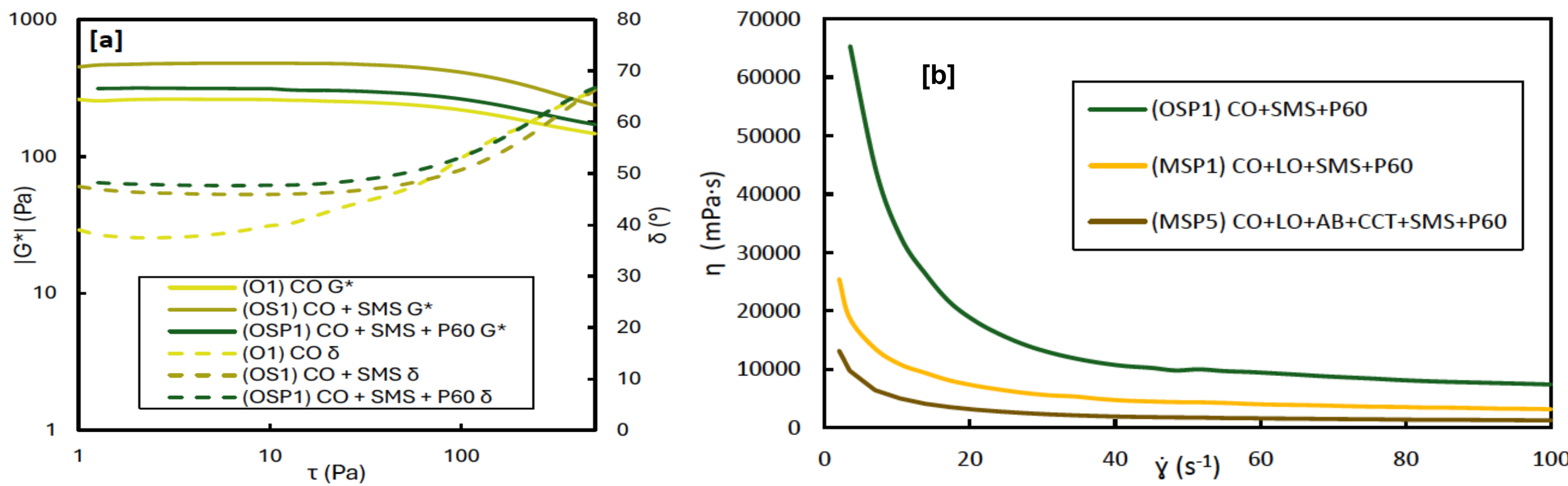


Figure 3: [a] Amplitude sweep of EC-CO oleogel (O1), and its counterparts with SMS (OS1) and SMS+P60 (OSP1); G^* (Pa) (full lines) and δ (dashed lines). [b] Viscosity of EC-SMS+P60 oleogels made with CO (OSP1), CO+LO (MSP1), and all oils (MSP5).

EC was essential for cold-cold emulsification and to obtain stable emulsions regardless of phase temperature. P60 reduced yield point and viscosity to values that allowed cold-cold emulsification (Figure 4) and reduced textural parameters to desirable values (Table 4). All emulsions were shear-thinning (Figure 4b), but only those containing CO (E1, ME1, ME5) were stable after one month. Therefore, **CO was key in obtaining stable EC oleogel emulsions.** Diluting CO decreased emulsion G^* (Figure 4a) and viscosity (Figure 4b) (E1 > ME1 > ME5); it also reduced stickiness, which is beneficial (E1 > ME5) (Table 4).

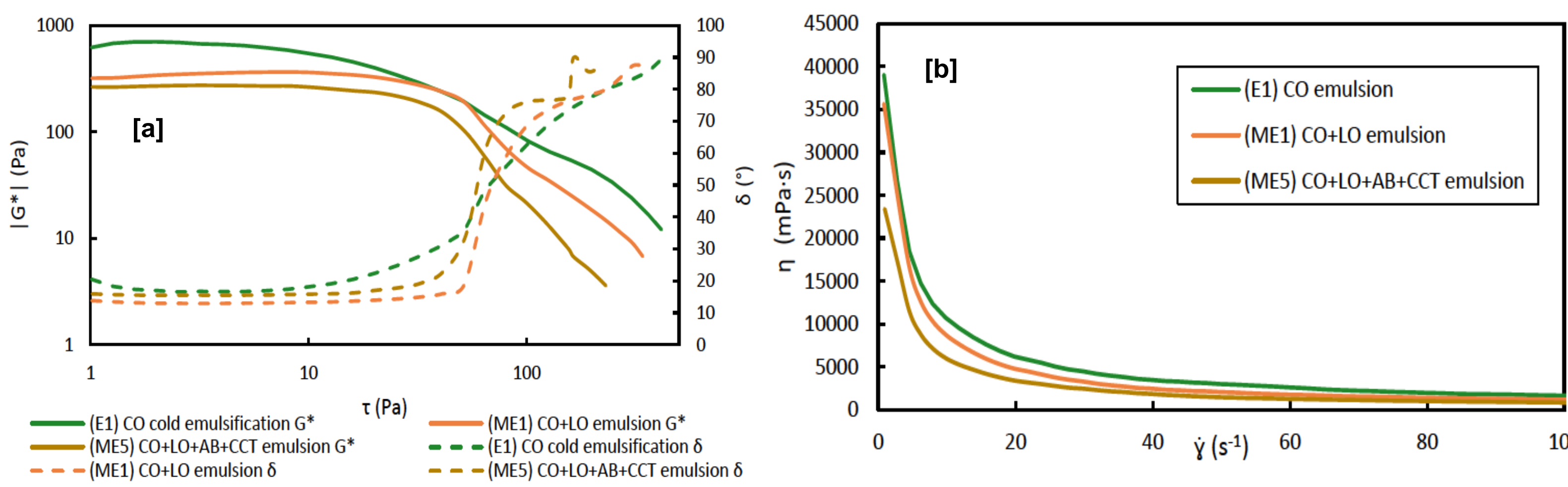


Figure 4: [a] Amplitude sweep of cold-cold emulsions E1 (CO); ME1 (CO+LO); and ME5 (CO+LO+AB+CCT). G^* (full lines) and δ (dashed lines). [b] Viscosity of cold-cold emulsions E1 (CO); ME1 (CO+LO); and ME5 (CO+LO+AB+CCT).

Table 4: Texture parameters of EC-CO oleogel emulsions E1 (SMS+P60); E3 (SMS only); E4 (no surfactant); and ME5 (all oils, SMS+P60). Mean $\pm$ SD of firmness (g), work of shear (g s), stickiness (g) and work of adhesion (g s).

Emulsion	Firmness (g)	Work of Shear (g s)	Stickiness (g)	Work of Adhesion (g s)
E1	169.26 $\pm$ 12.89	126.80 $\pm$ 11.54	-254.64 $\pm$ 20.78	-64.27 $\pm$ 4.92
E3	1700.89 $\pm$ 15.42	1090.00 $\pm$ 10.93	-2689.87 $\pm$ 27.40	-593.73 $\pm$ 4.18
E4	1030.15 $\pm$ 9.05	607.62 $\pm$ 7.45	-1710.10 $\pm$ 27.97	-366.61 $\pm$ 9.56
ME5	105.06 $\pm$ 6.60	80.45 $\pm$ 6.88	-117.94 $\pm$ 8.44	-33.31 $\pm$ 2.43

CONCLUSION It was shown for the first time that EC is suitable for cold-cold emulsification. A combination of castor oil diluted with suitable emollients and Polysorbate 60 were essential to adjust rheological parameters that facilitate emulsification. Additionally, this combination also resulted in emulsions of desirable texture.

[1] Davidovich-Pinhas, M. (2019) 'Oil structuring using polysaccharides', Current Opinion in Food Science, 27, pp. 29–35. doi: 10.1016/j.cofs.2019.04.006. [2] Tamburic, S., Fröhlich, J., Mistry, S., Fischer, L.J., Barbary, T., Bunyan, S. and Dufton, E. (2023) 'Sustainability by Reduced Energy Consumption during Manufacturing: The Case of Cosmetic Emulsions', Cosmetics, 10(5), pp. 132. doi: 10.3390/cosmetics10050132. [3] Gravelle, A.J., Davidovich-Pinhas, M., Zetzi, A.K., Barbut, S. and Marangoni, A.G. (2016) 'Influence of solvent quality on the mechanical strength of ethylcellulose oleogels', Carbohydrate Polymers, 135, pp. 169–179. doi: 10.1016/j.carbpol.2015.08.050. [4] Davidovich-Pinhas, M., Barbut, S. and Marangoni, A.G. (2015b) 'The role of surfactants on ethylcellulose oleogel structure and mechanical properties', Carbohydrate Polymers, 127, pp. 355–362. doi: 10.1016/j.carbpol.2015.03.085.