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"Silicone-Free Lip Balms: The Impact of Cooling Times and Temperatures on Performance"

Alex G. A. Salt[1], Divyashi Motwani[1], Veronika Kapsali[1], Asma Buanz[2], Tony O'Lenick[3], Thomas O'Lenick[3] and Milica Stevic[1]
[1]MSc Cosmetic Science; [2]Fashion Textiles/ MA Fashion, UAL, London College of Fashion, London; [3]Faculty of Engineering and Science, University of Greenwich, School of Science, Chatham, United Kingdom; [4]SurfaTech Corp., Lawrenceville, United States.

1. Introduction

Lip balms create a protective, moisture-retaining barrier using an anhydrous wax–oil–butter matrix [1]. Product texture and application quality depend not only on composition but also on processing conditions, especially cooling rate. Rapid cooling yields smaller, denser wax crystals and a firmer structure, while slower cooling allows larger spherulites to form, resulting in a softer texture [2].

While many formulations now include plant-based ingredients, non-biodegradable synthetic additives like oil-soluble multi-domain silicones (MDSi) remain prevalent due to their favourable oil-phase stability and distinctive sensorial characteristics [3]. However, the environmental persistence of silicones has led to regulatory scrutiny, with increasing restrictions on cyclic siloxanes such as D4, D5, and D6 [4,5], thereby increasing demand for sustainable alternatives. Biodegradable substitutes, such as polyglycerol esters (PGEs), offer promising emulsification and sensory profiles [6,7]. Yet, direct replacement of silicones with esters often requires reformulation to maintain performance [8], creating a cost and time barrier to sustainable innovation.

Although many studies focus primarily on ingredient selection, the potential of processing parameters—such as post-moulding cooling—as a compensatory strategy in silicone-free (SF) systems appears to be relatively underexplored. This study investigates whether modifying post-moulding cooling conditions enables the substitution of 1% multi-domain silicone (MDSi) with 1% polyglycerol ester (PGE) in an SF lip balm formulation, without altering the base composition. A silicone-based (SB) lip balm, cooled in the fridge (4 °C) for 30 minutes (SBFRI30), was used as the benchmark. SF lip balms were subjected to various cooling protocols, and instrumental performance metrics—hardness (h), pay-off (P), yield strain (γ_0), and melting enthalpy (ΔH)—were measured to evaluate whether SF formulations could replicate the performance of SB. This work aims to investigate how to create more sustainable lip balm formulations by focusing on processing rather than reformulation.

2. Materials and Methods

2.1. Multi-domain Silicone and Polyglycerol Ester

The SB lip balm formulation includes an MDSi polymer, (INCI: cetyl hexacosyl dimethicone), which features a polydimethylsiloxane (PDMS) backbone modified with a C16 (cetyl) hydrocarbon (liquid domain) and a C26 (hexacosyl) hydrocarbon (solid domain) (**Figure 1A**; **Table 1**). This multi-domain structure enhances flexibility and oil-phase stability in comparison to volatile, cyclic silicones [3]. The polymer has a melting point (T_m) of approximately 37 °C [9]. The SF lip balm formulation contains a PGE polymer (INCI: polyglycerol tetrastearate tetraisostearate polyester), which consists of a polyglycerol backbone with 50% isostearic and 50% stearic alkyl chains (**Figure 1B**; **Table 1**). This composition imparts oil solubility and flexibility, comparable to MDSi, with a T_m of approximately 40 °C [9].

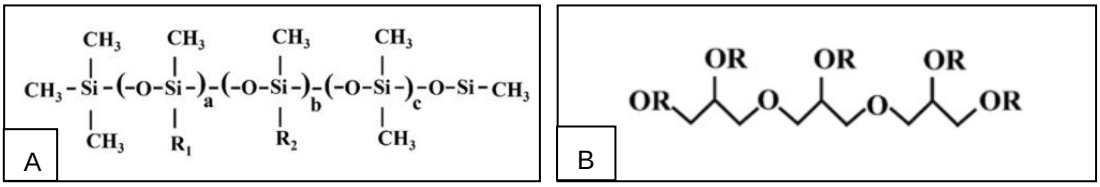

Figure 1. Structural formulae: **(A)** Multi-domain silicone structure; **(B)** Polyglycerol ester structure.

Table 1. Comparative structural characteristics of multi-domain silicone (INCI: cetyl hexacosyl dimethicone) and polyglycerol ester (INCI: polyglyceryl tetrastearate tetraisostearate polyester).

Multi-Domain Silicone				***Polyglycerol Ester***		
	R1 "Solid" Domain (a)	R2 "Liquid" Domain (b)	CH3 Silicone Region (c)		Alkyl (R) (Normalised) "Solid" Chain	Alkyl (R) (Normalised) "Liquid" Chain
Cetyl/hexacosyl Dimethicone	Hexacosyl (C26)	Cetyl (C16)	Methyl (C1)	Polyglycerol Tetrastearate Tetraisostearate Polyester	Stearic (C18)	Isostearic (C18)
The portion (a, b, or c) of the domain (solid, liquid, or silicone) in a molecule of MDSi polymer	2.5	1.5	8	Composition	50%	50%

2.2. Manufacturing Method and Formulation Compositions

A split metal lipstick mould was lubricated with ~0.1 mL castor oil per half-bullet, evenly distributed, and placed horizontally on a 45 °C hot plate. Phase A was combined in a beaker (**Table 2**). Phase B was premixed and added to Phase A. The combined phases were heated to 85 °C with magnetic stirring at 60 rpm, then homogenised using a T 18 digital ULTRA-TURRAX® (IKA, Germany), equipped with an S 18 N–19 G dispersing tool (IKA, Germany), at 9,000 rpm for 2 minutes. The formulation was poured into the assembled mould and immediately

transferred to the designated cooling condition and duration outlined in **Table 3**. After cooling, the excess formulation was removed from the mould surface, and the lip balms were demoulded, wrapped in cling film, and stored at 21 ± 1 °C.

Table 2. Composition of silicone-based and silicone-free lip balm formulations. Both formulations share the same base, differing only in the structuring agent used in Phase B.

Phase	*INCI*	*SB (% w/w)*	*SF (% w/w)*
A	Euphorbia Cerifera (Candelilla) Wax	3.00	3.00
	Copernicia Cerifera (Carnauba) Wax	4.00	4.00
	Cera Alba (Beeswax)	10.00	10.00
	Butyrospermum Parkii (Shea) Butter	29.70	29.70
	Caprylic/Capric triglyceride	12.00	12.00
	Ricinus Communis (Castor) Oil	34.30	34.30
B	Ricinus Communis (Castor) Oil	5.00	5.00
	Cetyl/hexacosyl Dimethicone	1.00	0.00
	Polyglycerol Tetrastearate Tetraisostearate Polyester	0.00	1.00
	Tocopherol acetate	1.00	1.00

Table 3. Assigned cooling conditions for silicone-based and silicone-free lip balm variants.

Cooling Condition		*Formulation Variant*	
Temperature (°C)	*Duration of cooling (min)*	*Silicone-based (SB)*	*Silicone-free (SF)*
Fridge (FRI): **4 ± 1**	20		✓ **(SFFRI20)**
	30	✓ **(SBFRI30)**	✓ **(SFFRI30)**
Room Temperature (RT): **21 ± 1**	25		✓ **(SFRT25)**
Freezer (FRE): **−20 ± 1**	7		✓ **(SFFRE7)**

2.3. Sample Preparation for Instrumental Characterisation

Standardised samples were prepared from each lip balm stick before mechanical and thermal testing, using a 3D-printed cutter [9] and blade. The lip balm divisions relative to each test are shown in **Figure 2**.

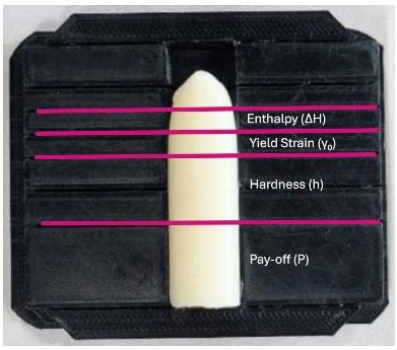

Figure 2. Representative lip balm samples used for instrumental characterisation.

2.4. Mechanical Characterisation

Hardness (h), pay-off (P), and yield strain (γ_0) were measured to characterise each lip balm variant. The averages and standard deviations (SDs) were calculated, with an SD acceptance threshold of ≤ 16%.

2.4.1. Hardness

Hardness (h) was measured using a TA.XTPlus texture analyser (Stable Micro Systems, Surrey, UK) fitted with a 2 mm needle probe. Ten 9-mm-long lip balm cuts, taken from the centre of the lip balm sticks (**Figure 2**), were individually centred under the needle probe and manually aligned. The final positioning was marked on the texture analyser platform with a marker pen for repeatable testing. The lip balms were tested using Exponent software (Stable Micro Systems, Surrey, UK) and the method "Comparison of hardness of two different lipstick batches by penetration with a 2 mm needle probe – an adaptation of ASTM Standard Method D 1321-95" [9]. The average force over 3.75–4.75 s was recorded to determine h (g).

2.4.2. Pay-off

Pay-off (P) was assessed using a TA.XTPlus texture analyser (Stable Micro Systems, Surrey, UK) configured with a vertical friction rig and a stationary vertical plate. Pre-weighed 11 × 13 cm pieces of Cotton Percale Neptune White fabric (Whaleys Ltd., Bradford, UK) were attached to the vertical plate. Ten 12-mm-long lip balm cuts, taken from the base of the lip balm sticks (**Figure 2**), were assessed per series. The samples, secured horizontally in a custom holder against the fabric, moved 45 mm at 15 mm/s over three cycles. The average P (mg) was calculated from the fabric's mass gain, and the friction pattern (force in g) was recorded using Exponent software (Stable Micro Systems, Surrey, UK).

2.4.3. Yield Strain

An oscillatory strain sweep was conducted using a HAAKE MARS iQ Air (Thermo Fisher Scientific, Hemel Hempstead, UK), configured with a Rotor P35/Ti/SE and a lower plate TMP35 S (serrated) (Thermo Fisher Scientific, Hemel Hempstead, UK), with a 2 mm gap. A 300-second equilibration time was initiated before testing. Deformation (γ) ranged from 0.01–10% at 1 Hz (6.2832 rad/s), with temperature controlled at 32 ± 1 °C. Five 4-mm-long lip balm cuts, taken from the top third of the lip balm (**Figure 2**), were assessed per series. The elastic modulus (G′,Pa), representing the material's elastic behaviour, and the loss modulus (G″,Pa), representing its viscous behaviour, were recorded. The yield strain (γ_0,%)—defined as the point where G′ drops by 10%—was calculated for each sample using RheoWin software (Hemel Hempstead, UK), and the average γ_0 ± SD was determined manually.

2.5. Chemical Characterisation

2.5.1. Enthalpy

Approximately 5 ± 1 mg of lip balm, scooped from the 4-mm-long cut section (**Figure 2**), was sealed in an aluminium pan with a small hole pierced in the lid and analysed using DSC (Discovery 2500, TA Instruments, Waters, Massachusetts, USA). The heating rate was

5 °C/min, from 20 to 200 °C, under an N_2 flow rate of 50 mL/min. Reference standard indium was used for cell constant and enthalpy calibration. Five samples were assessed per series. The average enthalpy (ΔH,J/g) was calculated from the first endothermic peak (24.85–41.85 °C).

2.6. Data Interpretation

A scoring system was implemented to evaluate the resemblance of SF variants to SBFRI30, with a total score (TS) based on percentage difference.

The calculation used to determine the difference was as follows:

The difference or d (%) = (F7 minus F6)/F6 x 100

The scoring system (**Table 4**) assigns a score from 1 to 5 for each parameter, based on percentage similarity to the SBFRI30 benchmark. A higher score indicates closer alignment of performance characteristics with SBFRI30. The maximum total score (TS) is 20.

Table 4. Scoring system of percentage differences across lip balm variants.

Difference, d (%)	***Score***
0–2	5
2–4	4
4–7	3
7–10	2
>10	1

3. Results

3.1. Mechanical and Chemical Results and Final Scores

The SB lip balm, cooled in the fridge for 30 minutes (SBFRI30), served as the benchmark for evaluating the SF lip balm variants. **Table 5** presents the average results for mechanical (h, P, γ_0) and thermal (ΔH) properties, while **Table 6** assigns a total similarity score (TS) out of 20. Although none of the SF samples fully replicated SBFRI30, SFFRE7 and SFRT25 achieved the highest scores (TS = 12 and TS = 11, respectively), indicating strong potential as silicone-free alternatives.

Table 5. Final results for the silicone-based benchmark and all silicone-free variants: hardness (h), pay-off (P), yield strain (γ_0), and enthalpy (ΔH).

		Test Parameters			
Formulation	***Cooling Condition***	**h (g)**	**P (mg)**	**γ_0 (%)**	**ΔH (J/g)**
SB	**FRI30**	75.63 ± 2.50	59.35 ± 3.88	0.09270 ± 0.01040	15.24 ± 2.05
SF	**FRI20**	76.84 ± 3.18	65.73 ± 7.81	0.10030 ± 0.00002	16.93 ± 0.98
	FRI30	79.32 ± 1.18	64.63 ± 7.80	0.10020 ± 0.00010	17.04 ± 0.60
	RT25	72.31 ± 1.88	59.45 ± 5.67	0.10030 ± 0.00004	17.30 ± 0.67
	FRE7	78.26 ± 1.23	60.49 ± 4.59	0.10030 ± 0.00002	18.49 ± 1.10

Table 6. Total similarity scores (out of 20) for the silicone-free variants compared to the silicone-based reference.

SF lip balms: Cooling Condition	*Score*
FRI20	9
FRI30	8
RT25	11
FRE7	12

To visualise overall trends and highlight the best-performing formulation, each figure in the following sections (3.2–3.5) presents two comparisons: the left panel shows all SF variants against the SB benchmark (SBFRI30), while the right panel focuses on SFFRE7—the top-scoring substitute—compared directly to SBFRI30.

3.2. Hardness

Hardness (h) was measured to assess the strength of the stick, specifically its resistance to needle probe penetration, which reflects how the product withstands application forces and external stresses. Hardness values ranged from 72.3 g (SFRT25) to 79.3 g (SFFRI30). SFFRE7 showed a 3.5% deviation, indicating slightly higher resistance to penetration than SBFRI30. Visual comparisons are shown in **Figure 3A–B**.

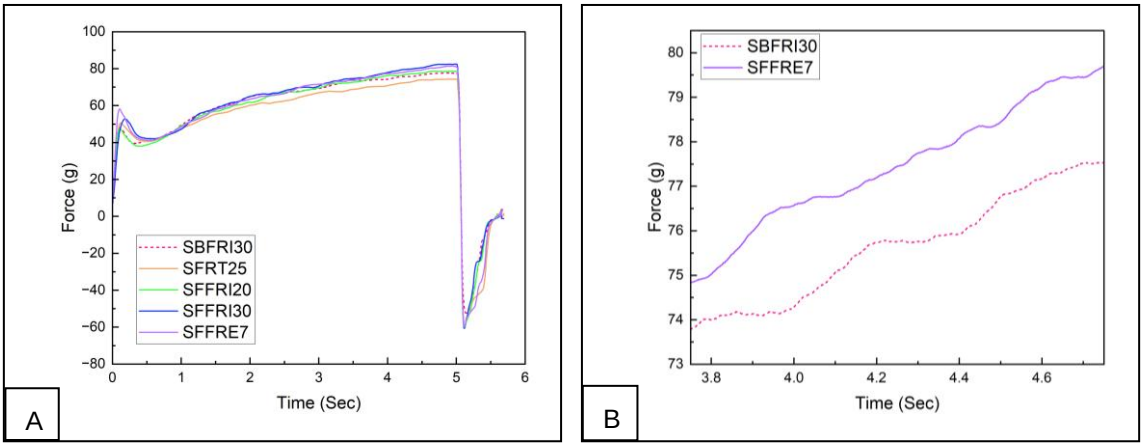

Figure 3. Hardness evaluation of lip balms showing the average force (g) as a function of time (sec): **(A)** Full data (0–6 sec) for all tested variants, including silicone-based (SBFRI30) and silicone-free systems under different cooling conditions. **(B)** Focused comparison between SBFRI30 and the silicone-free formulation cooled for 7 min at −20 °C (SFFRE7) in the analysis region (3.75–4.75 sec).

3.3. Pay-off

Pay-off (P) refers to the amount of material transferred from the lip balm stick to a given surface; a higher pay-off indicates greater product deposition. SBFRI30 produced the lowest pay-off overall (59.35 mg). SFRT25 was nearly identical (+0.17%), while SFFRE7 showed a slight but consistent increase (+1.9%). Visual comparisons are shown in **Figure 4A–B**.

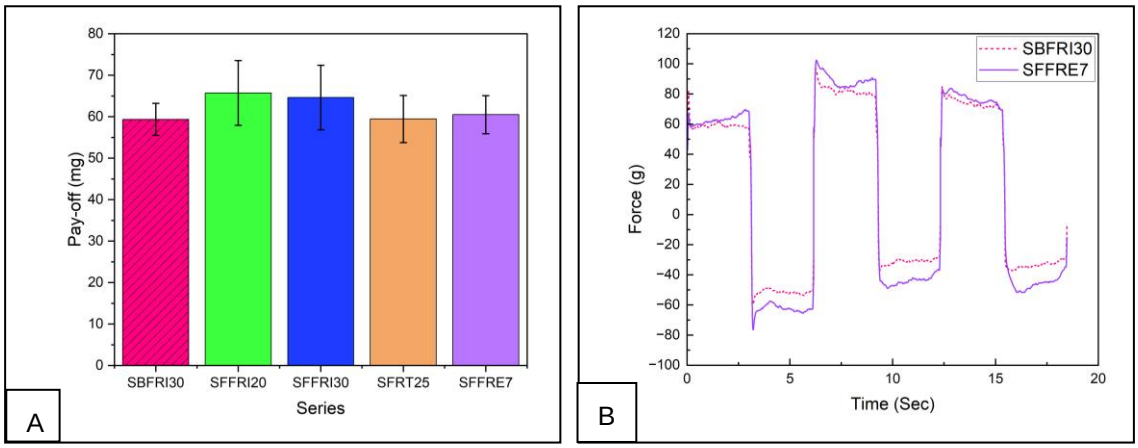

Figure 4. Pay-off evaluation of lip balm formulations: **(A)** Bar chart of final pay-off values (mean ± SD, mg) for all tested variants. **(B)** Kinetic friction profile (force, g as a function of time, sec), 0–19 sec, comparing SBFRI30 and SFFRE7.

3.4. Yield Strain

Yield strain (γ_0) is the amount of deformation (%) the lip balm undergoes at the point where irreversible (plastic) deformation begins. In this study, yield strain (γ_0) is defined as the strain at which the elastic modulus (G′, representing the material's stored energy and resistance to elastic deformation, measured in Pa) drops by 10%. A lower γ_0 indicates that the lip balm breaks and spreads more easily over the lips compared to a sample with a higher γ_0. All tested variants consistently showed G′ > G″, indicating predominantly elastic behaviour across all lip balms. The SF samples exhibited higher yield strain ($\gamma_0 \approx 0.100\%$) compared to SBFRI30 (0.093%), reflecting greater resistance to irreversible deformation. **Figure 5A–B** compares γ_0 values across variants.

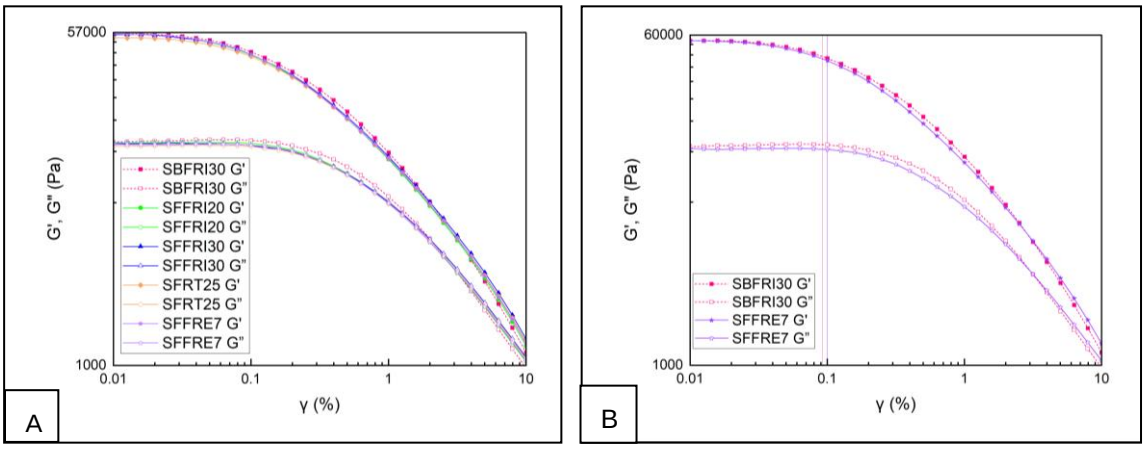

Figure 5. Rheograms showing G′ and G″ as a function of strain (γ, %) at 1 Hz and 32 ± 1 °C: **(A)** All formulation variants. **(B)** Focused comparison of SBFRI30 and SFFRE7. Vertical lines indicate yield strain (γ_0) where G′ drops by 10%.

3.5. Enthalpy

Differential scanning calorimetry (DSC) was used to assess the thermal behaviour of the lip balm samples by analysing the first melting peak. Enthalpy (ΔH) was calculated to evaluate the energy required for melting, providing insight into the internal crystalline structure and potential application performance. Higher enthalpy values indicate greater energy required to disrupt the structure, reflecting a higher degree of crystallinity and stronger molecular organisation. SBFRI30 exhibited the lowest ΔH (15.24 J/g), while all SF samples showed higher values. SFFRE7 demonstrated the largest deviation (+3.25 J/g), suggesting a denser crystalline structure. DSC curves are shown in Figure **6A–B.**

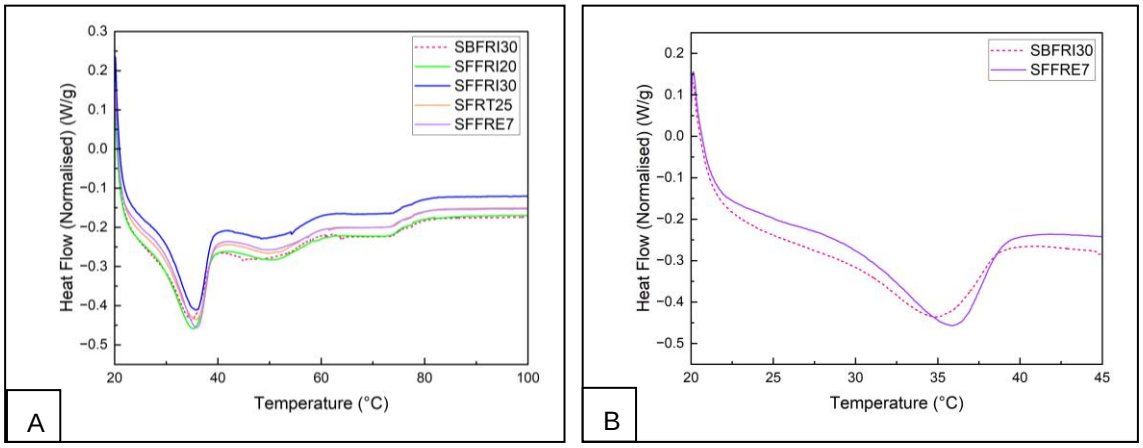

Figure 6. DSC thermograms showing normalised heat flow (W/g) as a function of temperature (°C) (Exotherm up): **(A)** Full profiles from 20–100 °C for all tested variants. **(B)** Focused comparison of the first melt peak (20–45 °C) for SBFRI30 and SFFRE7.

4. Discussion

The data collected through instrumental characterisation demonstrate that silicone-free lip balms can closely replicate the performance characteristics of MDSi-based lip balms by adjusting the cooling conditions during manufacture. Rapid cooling at −20 °C increased hardness, likely due to enhanced wax crystallisation through restricted spherulite growth [2,10], enabling control of firmness without altering the base formulation. Instrumental testing confirmed that these mechanical adjustments directly influenced attributes relevant to product application, such as resistance to penetration and material transfer.

Among the tested variants, SFFRE7 achieved the best balance of hardness and pay-off, improving product transfer without excessive softening of the overall structure—an important factor for lip balm usability and sensory feel [2,11]. Although SFFRE7 most closely matched the benchmark across mechanical properties, other variants also excelled in specific attributes, offering formulators flexibility to tailor cooling protocols to different performance priorities.

The increased yield strain observed in SFFRE7 likely reflects the wax-like deformability imparted by the polyglycerol esters, whose molecular structure promotes flexible yet resilient networks [6,7]. Thermal analysis further highlighted structural differences: the increase in enthalpy (ΔH) suggests a denser crystalline matrix, consistent with the organised packing of

structured alkyl chains and stronger intermolecular interactions characteristic of polyglycerol esters [6,9]. According to crystallisation principles outlined by Sato [10], such ordered structures require greater energy for phase transition, explaining the observed enthalpy increase. Importantly, this denser crystalline structure did not negatively affect mechanical performance and may enhance formulation robustness under variable storage conditions.

SFFRE7 demonstrated both competitive performance and manufacturing efficiency, achieving the highest total resemblance score (TS = 12/20) and offering a 76.6% reduction in cooling time. These findings show that fine-tuning cooling processes enables silicone-free formulations to closely match the instrumental performance characteristics of MDSi-based lip balms, supporting a practical and sustainable strategy for reducing reliance on synthetic silicones in cosmetic formulation [3,5].

5. Conclusion

This study investigated whether optimising post-moulding cooling could enable the replacement of a non-biodegradable silicone with a biobased, biodegradable polyglycerol ester in a lip balm formulation, without altering the base composition. Instrumental characterisation showed that although the silicone-free formulation did not fully replicate the benchmark, cooling adjustments significantly improved performance. The variant cooled at −20 °C for 7 minutes achieved the highest similarity while reducing production time by 76%, demonstrating that cooling optimisation is an effective strategy for developing more sustainable lip balm formulations. To fully validate these findings, a comprehensive sensory evaluation will be required to determine whether the silicone-free lip balms provide sensory attributes and user experience comparable to the silicone-based benchmark.

References

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