Instrumental Assessment of the Effectiveness of Silicone Replacement Materials in Lip Balms

Stevic, Milica[1]*; Naseem, Stefanie[1]; Tamburic, Slobodanka[1]; Buanz, Asma[2,3]; Rogaten, Jekaterina[1]; O'Lenick, Thomas;[4] O'Lenick, Anthony[4]

[1] Cosmetic Science Research Group, London College of Fashion, University of the Arts London, United Kingdom;

[2] Faculty of Engineering and Science, University of Greenwich, United Kingdom;

[3] School of Pharmacy, University College London, United Kingdom;

[4] SurfaTech, Lawrenceville, United States.

*Milica Stevic, 20 John Prince's Street London, W1G 0BJ, +447847219421, m.stevic@fashion.arts.ac.uk

Abstract

An emerging trend of silicone-free cosmetics has become evident since some silicone compounds are considered to have bio-accumulative and toxic properties. Lip balm manufacturing involves melting the ingredients into a homogenous mixture, followed by a process of cooling, during which crystallisation occurs. Melting and crystallisation determine the inner structure of lip balms and affect lip balm properties such as hardness, rigidity, and pay-off that are usually evaluated using sensorial testing. This study is an instrumental approach to selecting the best candidate for silicone replacement material.

Three series of lip balms with different ratios of carnauba and candelilla wax were studied. The functional agents in lip balms were either a multi domain silicone or one of four polyglycerol esters that served as the silicone replacement materials. Chemical characterisation of lip balms was performed using Thermal Gravimetric Analysis (TGA) and

Differential Scanning Calorimetry (DSC) while physical characterisation involved rheological and texture analysis (TA). The oxidative stability of the selected lip balms was measured.

The parameters assessed were melting temperature, melting enthalpy, hardness, yield stress, and induction time. Based on the melting point of the silicone and esters, as well as the melting enthalpy of the lip balms with silicones or esters obtained in DSC analysis, esters E3 and E4 were the best candidates to replace the silicone. Rheological and TA analyses of lip balms were consistent with the chemical findings.

This study provided an instrumental approach to exploring the effectiveness of silicone replacement with four polyglycerol esters in three different types of lip balms. This approach to the selection of materials can be applied before sensorial analysis.

Keywords: Lip balm; silicone replacement; polyglycerol esters; yield stress; hardness.

Introduction

Some silicones are considered to have persistent bio-accumulative and toxic (PBT) or very persistent very bio-accumulative properties (vPvB) properties [1]. PBT/vPvB substances have the potential to accumulate in the environment and cause effects that are unpredictable in the long-term and difficult to reverse. Therefore, there is a trend in the cosmetics industry to replace silicones with silicone alternative materials [2, 3, 4], without compromising the original sensorial properties of the product. Sensorial evaluation is a common approach to assess the effectiveness of silicone replacement materials in a product. While this approach allows reliable conclusions to be drawn, it is time-consuming and involves extensive planning of the experiment. Therefore, applying instrumental testing to select the best silicone replacement materials prior to sensorial testing can make the entire formulation process more efficient.

Lip balms (LBs) are mostly anhydrous mixtures composed of 60–70% oils and butters, 10–15% waxes, and 6–12% of other ingredients such as actives and preservatives [5]. They are produced by heating the ingredients and pouring the melted mixture into a mould, which is then left to cool for a specific period, during which the crystallisation of the mixture occurs. The type and concentration of waxes, polarity and viscosity of oils, and the cooling rate used are some of the factors affecting the crystal formation and ultimately the internal structure of lip products [6].

Polyglycerol esters (PGEs) are ingredients initially used in the food industry due to their ability to modify the process of crystallisation and the sensorial properties of the final products. A simplified formula of PGEs is given in Figure 1a, where the Rs are alkyl functional groups that determine properties of the compounds. PGEs were incorporated in lipid crystal systems [7, 8]their polarity and amphiphilic nature allowed them to be incorporated in cosmetic emulsions [9, 10]and oil-wax lipsticks, too [11, 12]. A multi-domain silicone (MDSi) is a silicone polymer comprising three clearly distinguishable regions: (a) solid alkyl, (b) liquid alkyl, and (c) silicone (Figure 1b).

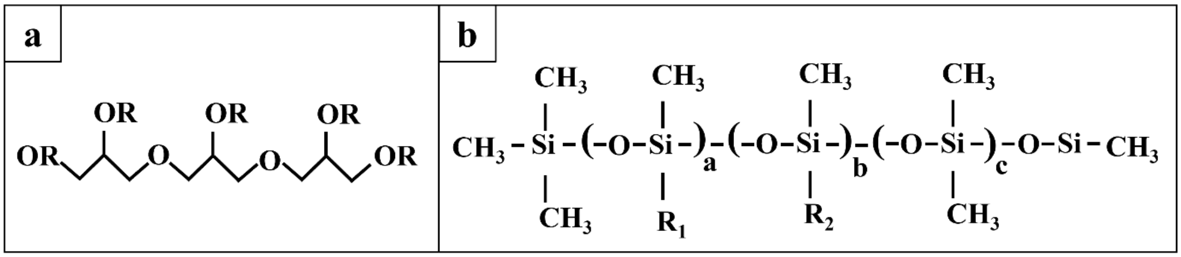

Figure 1. General formula: a polyglycerol ester **(a)** and a multi-domain silicone **(b)**. R, R1, and R2 are alkyl functional groups.

An instrumental approach to evaluating the effectiveness of PGEs to act as silicone replacement materials in LBs is suggested in this study. This approach consisted of two stages: (1) the selection of “the best fit” silicone replacement material achieved by performing chemical characterisation and (2) evaluation of the effectiveness of the selected silicone replacement material in LBs performed by applying physical characterisation. The selection considered the melting temperature of the materials and enthalpy of the LBs. The evaluation took account of the yield stress, hardness, and oxidative stability of LBs. The benefit of using this approach involved the selection of the best fit silicone replacement assessed at a chemical level. It aimed to make the selection of the formulating process more efficient and complement sensorial testing, rather than replacing it.

Materials and Methods

Materials

Candellila wax (Euphorbia cerifera cera) **(CLW)**, Carnauba wax (Copernicia cerifera cera) **(CRW)**, Beeswax (Cera alba) **(BW)**, Shea butter (Butyrospermum parkii) **(SB)**, Caprylic/capric triglyceride, and Castor oil (Ricinus communis oil) were purchased from Phoenix Natural Products (UK). Ester 1 (Polyglygerol Tetrabehenate Tetraisostearate Polyester, Carbon Number 20.2) **(E1)**, Ester 2 (Polyglygerol Tetrabehenate Tetraisostearate Polyester **(E2)**, Carbon Number 21.7), Ester 3 (Polyglygerol Tetrabehenate Tetraisostearate Polyester **(E3)**, Carbon Number 19.2), and Ester 4 (Polyglygerol Tetrastearate Tetraisostearate Polyester, Carbon Number 18.0) **(E4)** were donated by SurfaTech (Lawrenceville, USA). Silwax D221M (Cetyl/hexacosyl dimethicone) (**MDSi**) was donated by Siltech Corporation (Toronto, Canada). Polylactic acid (PLA) Ultimaker filament in a black colour, was purchased from Ultimaker (Ultimaker B.V., the Netherlands).

Methods

Lip balm manufacturing

Three different series of LBs: A, B and C, were formulated. Series A had 10% more CLW, series B had 10% more CRW, and series C had an equal amount of CLW and CRW. The formulation details are presented in Table 1. LBs were manufactured by adding all ingredients to a glass beaker and heating to 90 °C. The melted mixture was homogenised at 9,000 rpm for 2 minutes using a T18 digital Ultra-Turrax mixer (IKA, UK). The homogenised product was poured into a LB mould and cooled in a fridge to 5±1 °C for 20 minutes. Moulded LBs were placed in a lipstick container and kept at 22±1 °C for 24 hours. *LBs with silicone* were labelled AMDSi, BMDSi, and CMDSi; and *LBs with esters* were labelled AE1–AE4, BE1–BE4, and CE1–CE4, Table 1. *Series A* comprised following six LBs: A, AMDSi, AE1, AE2, AE3, and AE4; *Series B* following six LBs: B, BMDSi, BE1, BE2, BE3, and BE4; and *Series C* following six LCs: C, CMDSi, CE1, CE2, CE3, and CE4.

Table 1. Lip balm formulations.

Trade name	Base lip balm formula (g)		
	A	**B**	**C**
Candellila wax	2.64	2.40	2.40
Carnauba wax	2.40	2.64	2.40
Beeswax	9.70	9.70	9.70
Shea butter	26.50	26.50	26.50
Caprylic/capric triglyceride	11.00	11.00	11.00
Castor oil	38.76	38.76	38.76

	Lip balms with Silicone			Lip balms with Esters		
	AMDSi	**BMDSi**	**CMDSi**	**AE1-E4**	**BE1-E4**	**CE1-E4**
A, B, or C	✓	✓	✓	✓	✓	✓
MDSi	3 g	3 g	3 g	-	-	-
E1,2, 3, or 4	-	-	-	3 g	3 g	3 g

3D printing

Bespoke accessories to support sample preparation and physical characterisation were printed using an Untimaker S3 3D printer (Ultimaker, the Netherlands) and an Ultimaker Cura 4.9.1 software. The printing parameters were as follows: 0.06 mm layer height, 0.41 mm line width, 210 °C printing temperature, 55 mm/s print speed. The printing material was a PLA filament with a diameter of 2.85 mm.

Texture analysis

Texture analysis (TA) penetration tests were performed by adapting ASTM Standard method D1321-9517 using a TA.XT. Plus Texture Analyser (Stable Micro System, UK) with a needle probe diameter of 2 mm. The parameters were set as follows: 1 mm/s test speed, 5 mm LB penetration depth, and 5 g trigger force. A LB sample was placed below the probe in the centre of the base of the instrument. The resistance is the measurement of the hardness of the LB. It is expressed as force (g) and detected while the needle probe penetrated the sample. The force as a function of the penetration distance was recorded in Exponent software (Stable Micro System, UK). The LB hardness was the average force within the distance 3.5–4.5 mm.

Oscillatory strain sweep rheology

The rheological tests were conducted using a HAAKE MARS IQ Air Modular Advanced Rheometer (Thermo Fisher Scientific, Germany) with a stainless steel TMP35 serrated, parallel plate geometry. A LB sample was placed in the middle of the serrated platform. The applied method was an isothermal, oscillatory strain sweep mode at constant frequency. Angular displacement was $\phi = 1\text{x}10^{-5} – 0.05714$ rad, with a strain $\gamma = 0.0175–100\%$ at constant angular frequency of 6.2832 rad/s. The sample was first equilibrated for 10 minutes at 32±1 °C, with a 3-mm gap size. The test temperature remained constant (32±1 °C) during the test. HAAKE RheoWin software was applied to calculate elastic (storage) modulus (G'), viscous (loss) modulus G", and yield stress (τ).

Oxidative stability testing

Oxidation stability of the LBs was determined using a RapidOxy 100 instrument (Anton Paar, St Albans, U.K.). A sample with a mass of approximately 1 g was weighed using an analytical balance, evenly spread to cover the bottom of a glass sample holder and placed in the stainless-steel test chamber of the instrument. Rapid Small Scale Oxidation Test was completed under the accelerated conditions with a starting oxygen pressure of 700 kPa and temperature of 140 °C. The temperature was kept constant and the pressure continuously monitored. Due to the oxidation of the LB, oxygen was consumed which caused the pressure to drop. The parameter measured was the induction time. This was the time between the chamber first heating to the moment when a 10 % pressure drop was detected.

Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) was performed using a Discovery TGA (TA Instruments, Waters, LLC, USA). The instrument was calibrated according to the manufacturer's instructions for weight and temperature. Open aluminium pans were tared before the samples were loaded. The average sample weight was 3.0–5.0 mg. Samples were heated at a constant rate of 10 °C/min from 40 °C to 100 °C, and under the purge gas of nitrogen with a rate of 25 ml/min. TRIOS software (TA Instruments) was used to process TGA data, i.e., to calculate weight loss.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) experiments were conducted using a Q2000 DSC instrument (TA Instruments, Waters, LLC, USA). The instrument was calibrated with indium for cell constant and enthalpy prior to analysis. Nitrogen gas was purged with a flow rate of 50 ml/min. The average sample mass was 3.0–5.0 mg. The LB samples were placed in TA aluminum pans and enclosed with Tzero hermetic lids. A pin-hole was made in the middle of the lid for each sample prior to loading the instrument to allow for any volatiles to escape. The mass of the samples, empty pans, and lids were calculated. An empty pan with a lid were used to provide a reference. All samples were heated from 0 °C to 100 °C at a heating rate of 10 °C/min. The DSC profile was collected via TA Advantage software (TA Instruments) and the critical parameters including the peak of melting temperature (T_m) and transition enthalpy (ΔH) were analysed by TRIOS TA Instruments' software.

Results

Sample preparation

Ten LBs for each series A, B, and C (180 LBs in total) were formulated. Figure 2a depicts LBs series A. LBs were characterised within a couple of weeks after their production. For this project a single LB sample was used for both chemical and physical characterisation. A novel and bespoke method for sample preparation was developed to achieve this. A LB cutter (3DCut), Figure 2b, and a LB rheology guide (3DRheo), Figure 2c, were specifically designed and 3D printed to allow accurate sample preparation and characterisation. Each LB sample was prepared for analyses by placing it onto the 3Dcut (Figure 2d) and slicing it with a thin, sharp blade (Figure 2e). 3Dcut had grooves placed at specific distances to determine the thickness of each element of the LB, Figure 2f. Four individual LB elements formed after slicing a single LB and each one was used for the following analysis: Element 1–TA; Element 2–Rheology; Element 3–DCS and TGA; Element 4 – Oxidative stability. The number of replicas for each test was following: 10 for TA and rheological tests, 3 for TGA, DSC, and oxidative stability.

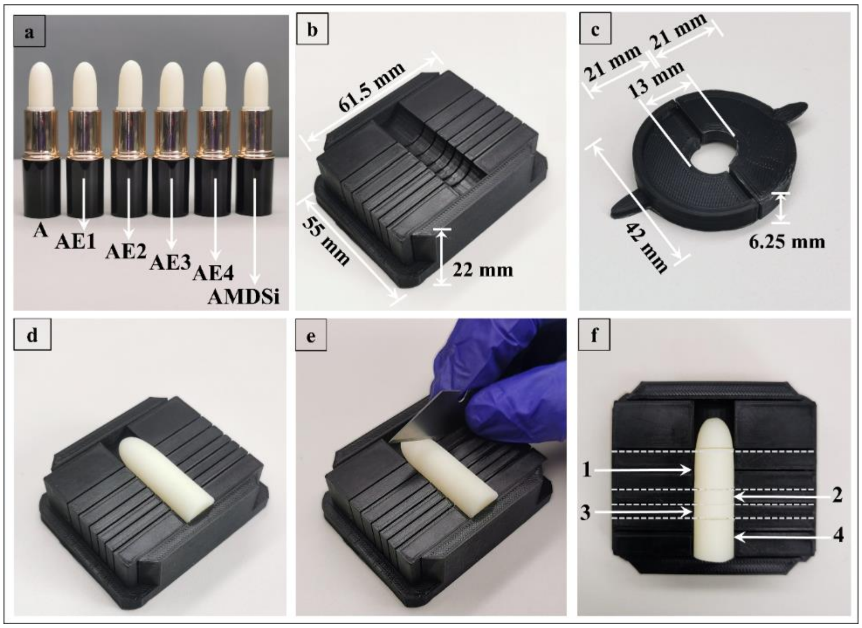

Figure 2. LBs series A **(a)**; 3DCut **(b)**; 3DRheo **(c)**; LB on a 3DCut **(d);** LB slicing – preparation for analyses **(e)**; sliced LB: elements 1–TA, element 2–Rheology, element 3–TGA/DSC, element 4–Oxidative stability **(f)**.

Chemical characterisation

Thermal analysis, TGA and DSC, was performed to determine which ester, E1, E2, E3 or E4, was the best silicone replacement material.

TGA

TGA analysis was conducted for SB, BW, CLW, CRW, MDSi, and E1-E4, which are referred to as raw materials (RMs) in this paper, and LBs for the temperature range 40–100 °C. The thermograms and weight loss (WL) of each material and LB is shown in Figure 3. CRW had a highest WL of 0.25%.

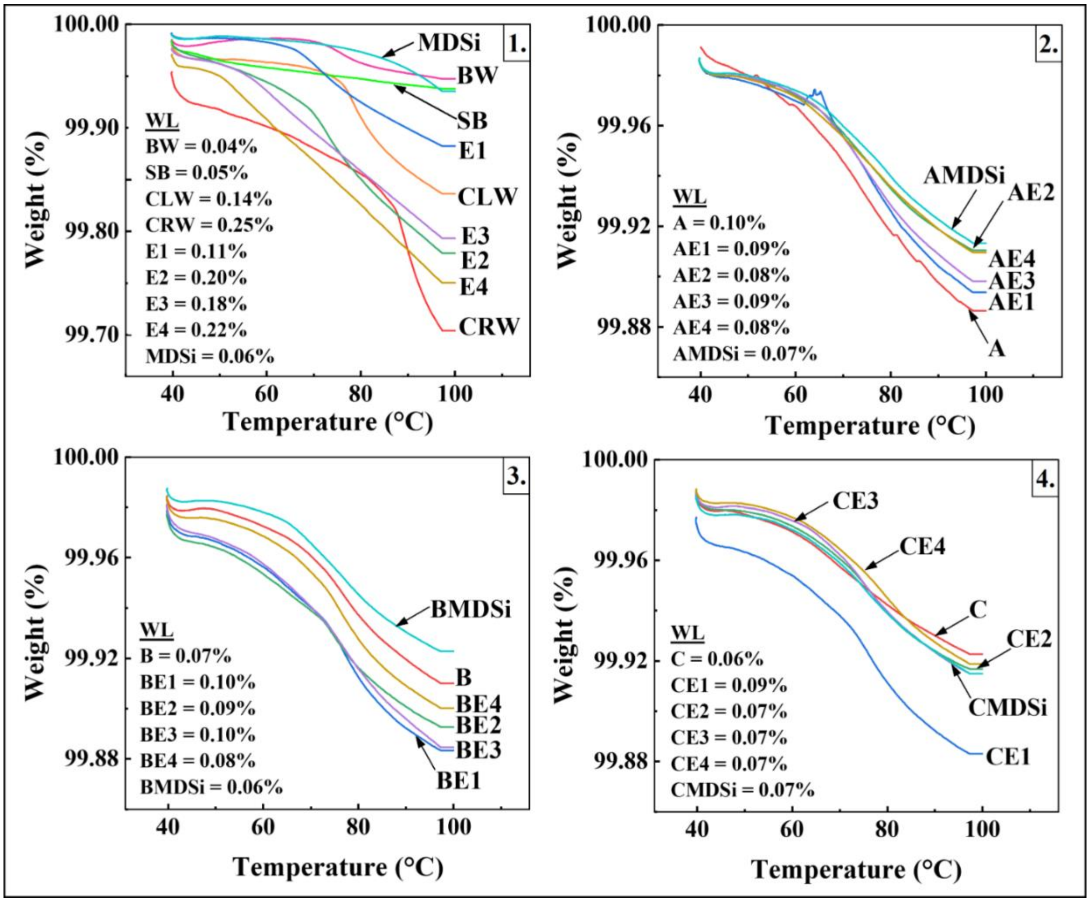

Figure 3. TGA profile and weight loss for: Raw materials **(1)**, LB A series **(2)**, LB B series **(3)**, LB C series **(4)**.

DSC

DSC thermograms obtained for RMs and all three LB series in the temperature range 0–100 °C with a scan rate of 10 °C/min are presented in Figure 4. Thermal profiles for RMs are shown is Figures 4.1 and 4.2. It was observed that BW, CLW, CRW, and E2 exhibited only one endothermic transition while the remaining materials showed two endothermic events. Figure 4.3 depicts how all four possible transitions (Tr 1–Tr 4) and for AE1 two DSC parameters were performed and calculated: (1) the melting maximum temperature of the transition (peak) (T_m) and (2) the mass normalised enthalpy (ΔH). Thermograms for all three LB series are presented in Figures 4.4, 4.5, and 4.6, respectively, and show that LBs undergo four endothermic transitions in the following temperature ranges: 0–14 °C, 28–44 °C, 45–60 °C, and 61–75 °C. The temperature of lips is 32 °C so a melting event taking place in the region 28– 44 °C (Transition 2) is of interest. Table 2 provides T_m and ΔH for all LB series for Transition 2.

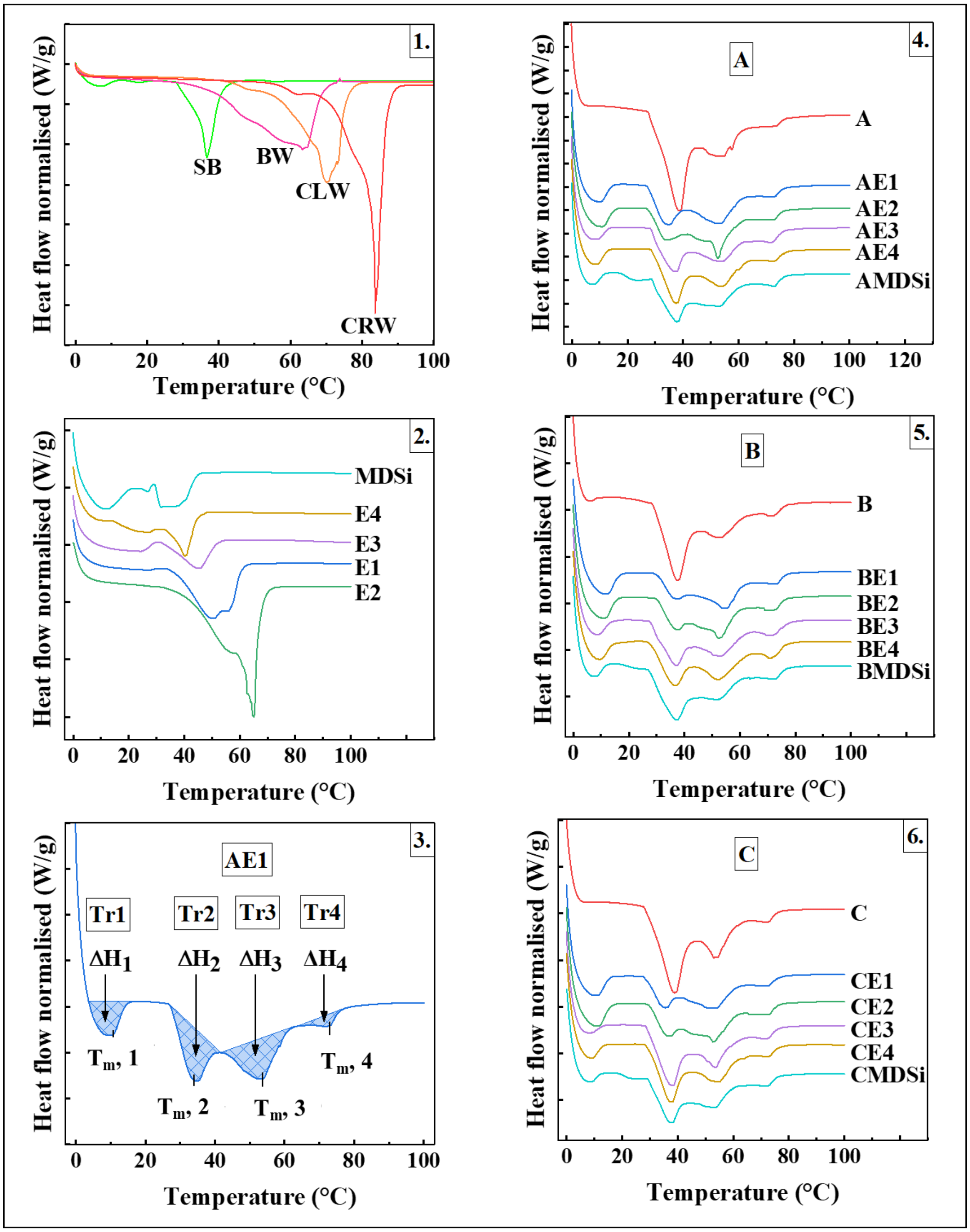

Figure 4. DSC profiles at 0-100 °C and scanning rate 10 °C/min. Raw materials **(1 and 2)**, determination of transition (peak) (T_m) and enthalpy (ΔH) for AE3 transitions (Tr 1-Tr 4) **(3)**, A series LBs **(4)**, B series LBs **(5)**, and C series LBs **(6)**.

Table 2. DSC parameters, the melting temperature of the transition (T_m) and the enthalpy (ΔH) for Transition 2 for all LB series (n=10).

		Transition 2	
		T_m (°C)	**ΔH (J/g)**
A	A	38.42 ± 0.61	15.88 ± 0.35
	AE1	33.71 ± 1.04	5.06 ± 0.61
	AE2	32.94 ± 0.65	2.68 ± 0.35
	AE3	36.54 ± 0.29	6.03 ± 0.68
	AE4	37.12 ± 0.53	7.28 ± 1.50
	AMDSi	37.48 ± 0.23	5.80 ± 0.89
B	B	37.32 ± 0.21	12.81 ± 0.40
	BE1	36.20 ± 0.52	2.11 ± 0.35
	BE2	36.33 ± 0.08	2.62 ± 0.34
	BE3	36.53 ± 0.35	5.77 ± 0.22
	BE4	36.28 ± 0.31	5.94 ± 0.80
	BMDSi	36.80 ± 0.61	8.14 ± 1.79
C	C	38.46 ± 0.13	14.39 ± 0.30
	CE1	34.72 ± 0.20	3.12 ± 0.53
	CE2	35.87 ± 0.15	2.71 ± 0.53
	CE3	37.40 ± 0.23	9.13 ± 0.48
	CE4	37.09 ± 0.15	8.24 ± 0.22
	CMDSi	36.96 ± 0.37	5.93 ± 0.94

Physical Characterisation

Assessment of the effectiveness of the selected silicone replacement esters was performed using TA and rheological characterisation.

TA

LB hardness is an important property that must be maintained during LB's application and storage. It is dependent of the temperature, so LBs were stored and the TA was performed at 22 °C. Hardness was measured using the penetration needle probe, Figure 5.1.Graphs of the force needed to be applied to penetrate 0–5 mm into LB series A, B, and C, as an average hardness curve (n=10), are presented in Figures 6.1-6.3. For each LB an average hardness for the region 3.5-4.5 mm was obtained and a summary of hardness values for all three series is presented in Table 3. From TA graphs and Table 3 it can be noticed that the addition of E2 and E1 improves, while the addition of E4 and DMSi lowers the hardness for all three series.

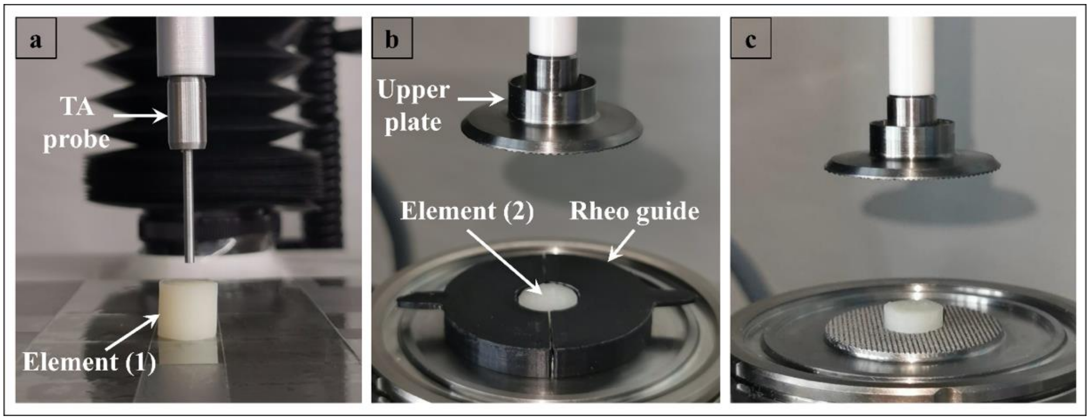

Figure 5. Lip balm sample: element 1 prior to TA testing **(a)**, positioning of the sample using Rheo guide **(b)**, and sample centered on the serrated plate prior to rheological testing **(c)**.

Rheology

To perform rheological analysis of stick products some researchers used parallel plates that are either sandblasted [13, 14], cross-hatched [15], or covered with sandpaper if smooth [16, 17]. The method used in this study involved using the 3DRheo to position the sample on the serrated plate, Figures 5b and 5c. Rheological profiles for all three LB series (n=10) are presented in Figures 6.4-6.6. Linear Viscoelastic Region (LVR) in oscillatory strain sweep tests is the region with low amplitude strains that indicates non-destruction of the sample. The length of the LVR is a measure of the stability of LBs. The yield stress was determined for all rheology profiles as the data point when G’ drops 10% from its initial value. Table 3 summarises three rheological parameters that determine the end of LVR.

Oxidative stability

LBs that were selected as the best silicone replacement fit were assessed using an oxidative stability kit. The drop in pressure is due to the oxidation of LBs. The parameter measured was the induction time. This was the time between the chamber first heating to the moment when a 10 % pressure drop was detected. The induction time for BE3, BE4, and CMDSi were 196±9 min, 201±10 min, and 208±1 min, respectively.

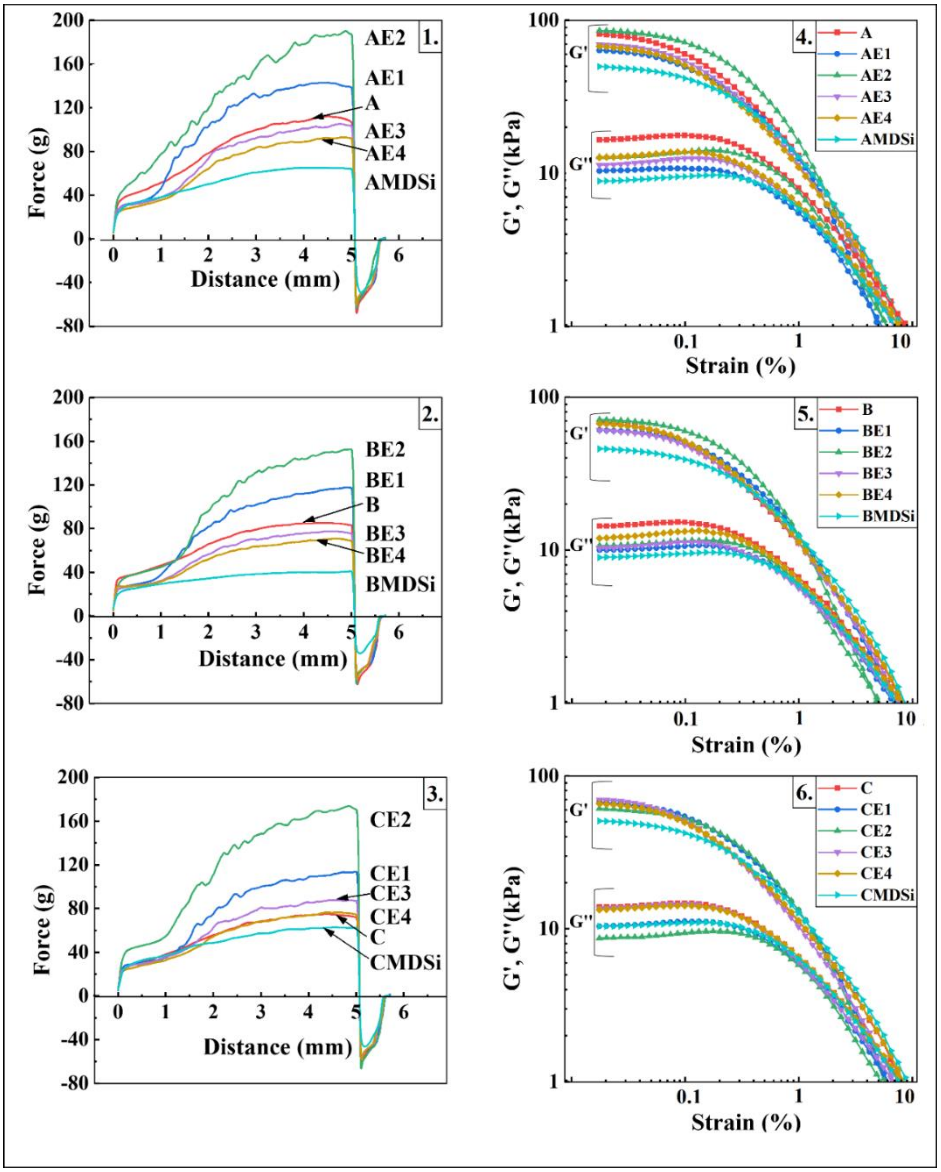

Figure 6. Texture analysis graphs for LB series: A **(1)**, B **(2)**, and C **(3)**. Rheology graphs for LB series: A **(4)**, B **(5)**, and C **(6).**

Table 3. LB series A, B, and C: average hardness data for the LB region 3.5–4.5 mm (n=10); and LVR elastic modulus (**G'**), yield stress (**τ**), and strain (**ɣ**).

Series	Lip balm	Hardness (g)	G' (kPa)	τ (Pa)	ɣ (10%)
A	A	108.47 ± 2.40	75.29 ± 3.44	48.49 ± 2.60	0.70 ± 0.03
	AE1	139.31 ± 2.59	64.66 ± 2.69	44.53 ± 4.71	0.72 ± 0.01
	AE2	178.26 ± 6.78	82.76 ± 5.51	62.67 ± 5.75	0.83 ± 0.04
	AE3	100.35 ± 1.88	66.25 ± 6.76	43.72 ± 5.22	0.72 ± 0.03
	AE4	89.60 ± 1.77	62.22 ± 7.33	40.40 ± 4.6	0.70 ± 0.03
	AMDSi	64.68 ± 0.57	47.93 ± 3.51	38.06 ± 2.45	0.86 ± 0.07
B	B	84.90 ± 1.02	63.22 ± 3.65	41.64 ± 4.11	0.71 ± 0.08
	BE1	112.16 ± 2.61	58.77 ± 2.29	44.38 ± 2.19	0.82 ± 0.04
	BE2	143.80 ± 4.10	69.01 ± 2.34	54.23 ± 4.39	0.86 ± 0.07
	BE3	75.52 ± 1.50	58.06 ± 4.86	40.22 ± 3.65	0.75 ± 0.03
	BE4	68.31 ± 1.53	62.92 ± 5.85	40.68 ± 4.26	0.70 ± 0.03
	BMDSi	39.90 ± 0.21	44.42 ± 3.29	36.44 ± 1.51	0.89 ± 0.04
C	C	73.82 ± 1.07	62.25 ± 2.43	40.01 ± 1.48	0.69 ± 0.03
	CE1	108.21 ± 2.15	64.12 ± 3.53	46.40 ± 4.19	0.79 ± 0.03
	CE2	164.24 ± 4.88	78.99 ± 1.68	66.87 ± 5.05	0.93 ± 0.08
	CE3	84.91 ± 2.13	65.31 ± 2.45	44.31 ± 5.01	0.75 ± 0.09
	CE4	74.00 ± 1.76	61.71 ± 4.26	39.72 ± 2.49	0.69 ± 0.01
	CMDSi	61.66 ± 0.69	48.77 ± 3.38	37.48 ± 3.11	0.83 ± 0.02

Discussion

LBs are comprised of a three-dimensional lipid crystal network formed in a two-staged mechanism: nucleation and crystal growth. Nucleation involves the organisation of monomers (e.g., triacylglycerols) into a domain to make a nucleus. The nucleus is the smallest crystal that can exist at a given temperature. External factors such as cooling rate [18], crystallisation temperature [15], and shear application during crystallisation [19], influence the formation of crystals. DSC transition enthalpy values can be used to characterise the strength of crystal networks in lipsticks [16].

TGA is often conducted as a DSC-complimentary method to ascertain how samples behave in the investigated temperature range. Figure 3 shows that in the region 38–100 °C the greatest weight loss was <0.25%. This may be attributed to the loss of moisture or volatile materials present in RMs or LBs. Krist [20] has previously reported the presence of volatile compounds in most RMs found in the LBs. TGA confirmed the absence of RM degradation in the temperature range investigated. This confirms that the DSC transitions were caused by phase transitions and not by sample degradation or evaporation [21].

The key consideration in DSC analysis are the parameters that indicate product performance such as the shape, size, and temperature of the peaks, Figure 4.3 [22]. The size and shape of DSC peaks are influenced by the concentration and distribution of the internal materials. The melting temperature of the peaks is dependent on the chemical composition of dominant components in the ingredient. The following trend of melting temperature maxima for RMs (Figure 4.1) is observed: T_m (SB) = 36.72 °C < T_m (BW) = 63.35 °C < T_m (CLW) = 70.07 °C < T_m (CRW)= 83.67 °C. This is consistent with the trend for melting point temperature ranges published by other authors: SB 34.0–38.0 °C [23, 24], BW 61.0–66.0 °C [25], CLW 68.5–72.5 °C [26], CRW 82.0–86.0 °C [26, 27].

The order of melting points for the silicone and esters (Figure 4.2) was the following: T_m (MDSi) = 37.38 °C < T_m (E4) = 40.53 °C < T_m (E3) = 45.71 °C < T_m (E1) = 50.86 °C < T_m (E2) = 65.10 °C. The general structural formulae for esters (PGEs) and MDSi are presented in Figure 1. Both groups of compounds have a solid alkyl region and a liquid alkyl region, and MDSi has the silicone region as well. The melting point of an ingredient or the final product, i.e., lip balm, depends on the type and ratio of the alkyl components.

In esters E1-E4, as the solid region, behenic (docosanoic, C22) acid with T_m= 80.0 °C, and stearic (octadecanoic, C18) acid with T_m = 69.3 °C, were used and as the liquid region, iso-stearic (16-methylheptadecanoic, i-C18) acid (liquid at room temperature) was used.

E1, E2, and E3 contain behenic and iso-stearic acid in the ratios 56:44, 78:22, and 30:70, respectively. Due to behenic acid having the highest melting point of all three carboxylic acids, the ester with the highest portion of behenic acid (E2) had the highest melting point (65.10 °C), and the one with the highest portion of iso-stearic acid (E3) had the lowest melting point (45.71 °C). E4 contains stearic acid and iso-stearic with a ratio of 50:50 and T_m determined from th DSC data was 40.53 °C.

The MDSi had a silicone polymer backbone with three regions: (a) liquid alkyl, (b) solid alkyl, and (c) a silicone. The ratio was a:b:c=2.5:1.5:8. The solid region was cerotic (hexacosanoic, C26) acid with T_m = 87.70 °C, and the liquid region was palmitic (hexadecenoic, C16) acid. The cerotic and palmitic ratio was 50:50, and the Tm of determined from the DSC data was 37.38 °C.

Based on the similarity of RMs' T_m, it can be concluded that E4 (40.53 °C), followed by E3 (45.71 °C), are the best MDSi (37.38 °C) replacement candidates.

From DSC of LBs (Figure 4.4-4.6), four peaks in four different temperature regions are observed. The temperature of the lips is around 32 °C so it is of the interest to study Transition 2 or the second peak (28–44 °C). Transition 2 enthalpy values for A, B, and C (Table 2) were 15.88 J/g, 12.81 J/g, and 14.39 J/g, respectively, and these values drop with addition of esters and MDSi. This is probably because the LB internal structure becomes weaker when these materials are added.

Transition 2 enthalpy value is an indication of how much heat is needed to melt LB during application. Therefore, the LB with ester with the closest enthalpy value to the MDSi LB is likely to be the best silicone replacement material. From Table 2 based on the closest enthalpy values following replacements can be found: AMDSi: BE4, BE3, and AE3; BMDSi: CE4, AE4, and CE3; CMDSi: BE4, BE3, and AE3.

Based on the thermal analysis it can be concluded that the best MDSi replacement materials were E4 and E3 in the LB application temperature range.

G’ and G’’ are indicators for the solid- and viscous-like behaviour of the LBs, respectively, while the τ represents the critical stress required to shift the viscoelastic response of the network. An oscillatory strain sweep test was performed at 32 °C, to imitate the temperature of lips. At 32 °C LBs were midway through thermal Transition 2 as observed from their thermal profiles, Figures 4.4-4.6. At low strain amplitudes, in the LVR, LBs were dominated by an elastic behaviour (G’>G”) and dependent solely on their structure rather than the strain. This is a characteristic of lip products [16, 17, 28]. In this paper it was found that LBs with different esters (PGEs) have different hardness, elastic modulus, and yield stress and this was observed throughout all three series. Even though crystallinity was not measured in this study, the hypothesis is that different esters produce LBs with different crystallinity. Indeed, Shimamura, et al. [29] and Saitou, et al. [30] have demonstrated that PGEs of different fatty acids greatly influence the promotion or retardation of crystallization.

The hardness data in Figure 6 and Table 3 show that the hardness of all three base formulations, A, B, and C decreases with the addition of MDSi and increases when adding E1 and E2. Therefore, E1 and E2 are not the most suitable silicone replacement candidates.

Yield value of LB is the amount of pressure/force needed in order to break its original structure. When applying LB on the lips, it melts leaving the LB layer, so yield stress is the monitored parameter when using rheology. From Table 2 it is observed that for yield stress the closest values were following: AMDSi: AE4; BMDSi: BE3 and BE4; CMDSi: CE4.

It can therefore be concluded based on texture analysis and rheological parameters that E4, followed by E3 are the best candidates for silicone replacement materials.

Since chemical and physical characterisation found that E4 and E3 were the best MDSi replacement materials, oxidative stability testing was performed for selected LBs containing E3 and E4 (BE3 and BE4) and CMDSi, as the LBs with an equal amount of high temperature melting waxes. The values for the induction time were close, so whichever ester is selected the oxidative stability will not be affected.

Based on the physical characterisation and stability testing, the sample E4 followed by E3 provide LBs of similar quality to the silicone-based LBs with equal amount of carnauba and candelilla wax.

Conclusion

This study describes an instrumental approach to evaluating the effectiveness of polyglycerol esters in the process of selection of silicone replacement materials in lip balms. Using thermal techniques, the melting temperature, and melting enthalpy, E4 and E3 were selected as "the best fit" silicone replacement materials which was in line with TA and rheology findings. The benefit of using this approach involves the selection of the best silicone replacement material assessed at the chemical level. It aims to make the formulating process less time-consuming and to complement sensorial testing rather than replace it.

Acknowledgments. Authors would like to thank Anton Par, UK for providing equipment for testing oxidative stability.

Conflict of Interest Statement. NONE.

References

[1] Health and Safety Executive, "Initial assessments of some substances recently recommended by ECHA for inclusion in Annex 14 of EU Reach," U.K., 2021.

[2] S. Bom, H. Ribeiro and J. Marto, "Choosing sustainable alternatives for cosmetic emollients: Sustainability vs rheological performance," in Iberian Meeting on Rheology, Switzerland, 2019.

[3] O. Kunik, D. Saribekova, L. Saleba, H. Ivakhenko and Y. Panchenko, "Research on physical and chemical properties of cosmetic emulsions of oil in water type based on polyorganosyloxanes and their alternative substitute," Chemistry & Chemical Technology, vol. 13, no. 4, pp. 526-534, 2019.

[4] S. Bom, M. Fitas, A. Martins, P. Pinto, H. Ribeiro and J. Marto, "Replacing synthetic ingredients by sustainable natural alternatives: A case study using topical O/W emulsions," Molucules, vol. 25, no. 21, pp. 4887-4905, 2020.

[5] N. Morante, "Ingredients for creating the next greatest lipstick," in Harry's cosmeticology, 9th ed., M. Rosen, Ed., U.S.A., Chemical Publishing Company, 2015, pp. 586-604.

[6] M. Shimizu, Y. Nomura and H. Bui, "Effect of cosmetic oils on lipstick structure and its deposit," in Surface Science and Adhesion in Cosmetics, K. Mittal and H. Bui, Eds., Scrivener Publishing LLc, 2021, pp. 35-72.

[7] N. Garti and A. Aserin, "Effect of emulsifiers on cocoa butter and chocolate: Rheology, polymoprhism, and bloom," in Cocoa butter and related compounds, N. Garti and N. Widlak, Eds., AOCS Press, 2012, pp. 275-305.

[8] E. Daels, A. Rigolle, K. Raes, J. De Block and I. Foubert, "Monoglycerides, polyglycerol esters, lecithin, and their mixtures influences the onset and non-isothermal fat crystallistionn in a concentraion dependent manner," European Journal of Lipid Science and Technology, vol. 117, no. 11, pp. 1745-1753, 2015.

[9] M. Taylor, "Stabilisation of water-in-oil emulsions to improve the emollient properties of lipstick," University of Birmingham, 2011.

[10] A. Beri, J. Norton and I. Norton, "Effect of emulsifier type and concentration, aqueous phase volume and wax ratio on physical, material and mechanical properties of water in oil lipsticks," International Journal of Cosmetic Science, vol. 35, no. 6, pp. 613-621, 2013.

[11] B. Park and C. Ha, "The properties of oil-wax gels with changing lattice structure of wax crystal," Materials Science, vol. 569, pp. 143-150, 2012.

[12] H. de Clermont-Gallerande, S. Abidh, A. Lauer, S. Navarro, G. Cuvelier and J. Delarue, "Relations between the sensory properties and fat ingredients in lipsticks," Oliseeds & fat Crops and Lipids, vol. 25, no. 5, 2018.

[13] A. Beri, R. Pichot and I. Norton, "Physical and material properties of an emulsion-based lipstick produced via a continuous process," International Journal of Cosmetic Science, vol. 36, no. 2, pp. 148-158, 2013.

[14] G. Buitimea-Cantúa, S. Serna-Saldívar, E. Pérez-Carrillo, T. Silva, D. Barrera-Arellano and N. Buitimea-Cantúa, "Effect of quality of carnauba wax (Copernica cerífera) on microstructure, textural, and rheological properties of soybean oil-based organogels," LWT, vol. 136, p. 110267, 2021.

[15] I. Tavernier, C. Doan, D. de Walle, S. Danthine, T. Rimaux and K. Dewettinck, "Sequential crystallisation of high and low melting waxes to improve oil structuing in wax-based oelogels," Royal Socety of Chemistry, vol. 7, pp. 12113-12125, 2017.

[16] S. Pan and N. Germann, "Thermal and mechanical properties of industrial benchmark lipstick prototypes," Therrmochimica Acta, vol. 679, p. 178332, 2019.

[17] S. Pan, S. Sivanathan, G. Kiepe, T. Kiepe and N. Germann, "Candidate formulations for a sustainable lipstick supplemented with vitamin D3: Effects of wax type and concentration on material properties," Industrial & Engineering Chemistry Research, vol. 60, no. 5, pp. 2027-2040, 2021.

[18] S. Jana and S. Martini, "Effect of high-intensity ultrasound and cooling rate on the crystallization behavior of beeswax in edible oils," Journal of Agricultural and Food Chemistry, vol. 62, no. 41, pp. 10192-10202, 2014.

[19] T. Tran and D. Rousseau, "Influence of shear on fat crystallization," Food Research International, vol. 81, pp. 157-162, 2016.

[20] S. Krist, Vegetable Fats and Oils, Cham, Switzerland: Springer, 2020.

[21] L. Budai, I. Antal, I. Klebovich and M. Budai, "Natural oils and waxes: Studies on stick bases," Journal of Cosmetic Science, vol. 6, no. 2, pp. 93-101, 2012.

[22] Mettler Toledo, "Characterization of lipstick by thermal analysis," 2022. [Online]. Available: https://www.mt.com/gb/en/home/campaigns/product-organizations/ana/GLEN/LAB_moisture_1704.html. [Accessed 17 May 2022].

[23] J. Iyasele, N. Oseni and O. Uwadia, "Rheological and microstructural properties of thermal and mechanically treated shea butter," Physical Science & Biophysics Journal, vol. 3, p. 000116, 2019.

[24] S. Maranz, Z. Wiesman and N. Garti, "Phenolic consituents of Shea (Vitellaria paradoxa) Kernels," Journal of Agricultural and Food Chemistry, vol. 51, no. 21, pp. 6268-73, 2003.

[25] H. Hepburn, R. Bernard, B. Davidson, W. Muller, P. Lloyd, S. Kurstjens and S. Vincent, "Synthesis and secretion of beeswax in honeybees," Apidologie, vol. 22, pp. 21-36, 1991.

[26] W. Tinto, T. Elufioye and J. Roach, "Waxes," in Pharmacognosy: Fundamentals, applications and strategies, S. Badal and R. Delgoda, Eds., Academic Press, 2017, pp. 443-455.

[27] I. Bayer, D. Fragouli, P. Martorana, L. Martidonna, R. Cingalani and A. Athanassiou, "Solvent resistant superhydrophobic films from self emulsifying carnauba wax-alcohol emulsions," Soft Matter, vol. 7, p. 7939, 2011.

[28] B. Maktabi, M. Liberatore and G. Baki, "Meadowfoam seed oil as a natural dispersing agent for colorants in lipstick," International Journal of Cosmetic Science, vol. 43, no. 4, pp. 484-493, 2021.

[29] K. Shimamura, S. Ueno, Y. Miyamoto and K. Sato, "Effects of polyglycerine fatty acid esters having different fatty acid moieties on crystallisation of palm stearin," Crystal Growth & Design, vol. 13, no. 11, pp. 4746-4754, 2013.

[30] K. Saitou, R. Homma, N. Kudo, Y. Katsuragi and K. Sato, "Retardation of crystallization of diacylglycerol oils using polyglycerol fatty acid esters," Journal of the American Oil Chemists' Society, vol. 91, no. 5, pp. 711-719, 2014.