Determination of Lipstick Authenticity Parameters

Stevic, Milica[1]*; Bei, Ran[2]; Naseem, Stefanie[1]; Rogaten, Jekaterina[1]; Nahar Hoque, Tanzina[2]; Tamburic, Slobodanka[1]; Buanz, Asma[2,3]

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

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

[3] Faculty of Engineering and Science, University of Greenwich, United Kingdom.

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

Abstract

Counterfeit medicine and cosmetics are available on the market despite the joint effort of corporations, e-commerce platforms, and the regulatory authorities to "fight the fakes". This could be due to the lack of quick and reliable analytical methods for identifying counterfeit products. Techniques that perform physicochemical characterisations are the most reliable way to detect counterfeit cosmetics. However, this is costly and time-consuming therefore a more efficient approach to determine counterfeit cosmetics is beneficial. The aim of the study was to show how physical characterisation parameters such as hardness and yield stress could be used as a tool to authenticate stick-based products.

MAC lipsticks from seven vendors were characterised chemically applying Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). Physical characterisation was performed applying rheology and texture analysis and statistics were used to determine whether the mean difference between authentic and counterfeit lipsticks was significant.

A remarkable difference in FT-IR spectra and thermograms of authentic and counterfeit lipsticks was identified. As such, chemical characterisation was applied to authenticate the

lipsticks. Rheological and texture data for yield stress and hardness for all lipsticks was collected and processed using statistical analysis. The effect size in hardness and yield stress between authentic and counterfeit lipsticks was then calculated.

This study explored the application of physical parameters (yield stress and hardness) to authenticate lipsticks. The authenticity parameters approach proposed could be applied to efficiently detect counterfeit lipsticks.

Keywords: Lipstick; authenticity; counterfeit; yield stress; hardness

Introduction

Lipstick is a lipid-based solid mixture whose functions are to provide lasting colour with different finish effects and protect the lips. A matte lipstick is mainly comprised of emollients (50–70%), waxes (15–25%), pigments (5-10%), plasticisers, and a minimum amount of additive substances [1, 2]. The general methods to authenticate lipsticks include packaging inspection, sensorial testing, physical and chemical characterisation of the product.

The waxes mainly employed in lipsticks are beeswax and carnauba wax, whose peak melting temperatures are in the range of 55-70 °C and 70-85 °C, respectively [3]. Moreover, the content of waxes contributes to the viscosity change, which is an essential parameter to characterise the physical property of lipsticks [4]. Therefore, different types and contents of waxes in lipstick formulation reflect distinctive melting behaviours, hardness, viscosity, and spectral peaks, thus facilitating the identification and discrimination of authentic and counterfeit lipsticks in a reliable and reproducible way.

Traditional methods for the characterisation of lipsticks include HPLC, GC, thin-layer chromatography (TLC), and paper chromatography (PC). TCL and PC with visualization under UV light have utilised forensic analysis to identify lipstick samples [5]. Furthermore, spectroscopy techniques are extensively applied to characterise lipsticks, which are superior in discriminating power and rapid screening. Salahioglu & Went [1] have established a rapid trace detection of 69 lipsticks from different brands through Raman spectroscopy, which

provided informative data in lipstick differentiation. Nevertheless, this technique has limitations in the analysis of red lipsticks and intense fluorescent samples. Zhang et al. [6] have improved the discriminating power of Raman spectroscopy in lipstick identification through chemometric methods. Comparable analysis of four spectroscopic techniques has demonstrated that IR spectroscopy has the advantages of no destruction to samples, rapid analytical sifting, and high reproducibility [7]. Gładysz, Król, & Kościelniak [8] have developed an attenuated total reflection (ATR) technique with principal component analysis (PCA) and cluster analysis (CA) to characterise lipsticks with similar compounds, which indicates an extensive application of ATR in counterfeit differentiation. Despite difficulty in determining a specific substance, ATR-FTIR is helpful to prove the presence of specific functional groups in lipstick formulation [2]. Furthermore, Sharma, Kumar, & Bharti [9] have verified the presence of various compounds (e.g., aliphatics and silicates) through ATR-FTIR and investigated the shift of spectral peaks under temperature change.

Discrimination of counterfeit lipsticks can be investigated by thermo-mechanical properties in addition to these methods. Pan & Germann [10] have performed systematic research into the thermal and rheological properties of lipsticks with superior prototype-dependent results. The melting profiles of DSC analysis have been evaluated as fingerprinting to identify lipsticks [11, 12]. Thermal transition obtained in the DSC method and penetration index from the texture analysis are closely associated with the physicochemical properties of lipsticks in different bases of wax [13].

The past eight years have witnessed an increase in MAC users, revealing that MAC has become a leading brand with the sixth largest number of users in the UK [14]. In particular, the number of MAC lipsticks users ranked first in the whole line of MAC products (ibid.). At the same time, MAC lipsticks have been plagued by counterfeits. Therefore, MAC lipsticks (shade Ruby Woo) purchased from different vendors were chosen to be investigated in this study. A combination of chemical, physical, and statistical analysis was used to develop a tool for to predict the authenticity of lipsticks quickly and reliably.

Materials and methods

Materials

MAC Retro matte lipsticks of the Ruby Woo shade were purchased from seven different vendors. The MAC retail store (St Pancras, London, UK) and MAC Cosmetics official website were considered authentic. The remaining lipsticks were obtained from the following online platforms: Notino (**N**), eBay (**EB**), Onbuy (**OB**), Ali Express (**AE**), and DH Gate (**DH**). "In store" refers to the lipsticks bought in the MAC store and "online" refers to the remaining lipsticks. **Figure 1a** shows individual lipsticks in their packaging and in **Figure 1b** individual lipstick bullets are shown. Carnauba wax and Beeswax were purchased from Sigma-Aldrich. Polylactic acid filament (Ultimaker PLA) in a black colour was purchased from Ultimaker (Ultimaker B.V., Netherlands).

Figure 1. MAC Retro lipsticks (Ruby Woo shade): in packaging **(a)** and lipstick bullets **(b)**.

Methods

Fourier Transform Infrared Spectroscopy (FT- IR)

The spectra of raw materials and lipsticks were obtained using a Spectrum 100 FTIR Spectrometer (PerkinElmer 100, USA), in an Attenuated Total Reflectance mode, using Spectrum Express software (PerkinElmer 100, USA). Prior to every measurement the

instrument sample stage and probe were cleaned with ethanol. Background scanning was conducted in the 65–4000 cm^{-1} range, with an average of 16 scans, and a resolution of 8 cm^{-1}. After obtaining an expected spectrum of a background, the sample was loaded to cover the crystal in the middle of sample stage. The spectra of all samples were displayed by taking wavelength as the x-axis and percentage transmission (%T) as the y-axis.

Thermogravimetric Analysis (TGA)

TGA was performed using a Discovery TGA (TA Instrument, Waters, LLC, USA). The instrument was calibrated according to the manufacturer's instructions for weight and temperature. Open aluminium pans were tared before loading the samples. The average sample weight was 3–5 mg. Samples were heated at a constant rate of 10 °C/min from room temperature to 120 °C, and under the purge gas of nitrogen with a rate of 25 ml/min. TRIOS software (TA Instrument, Waters, LLC, USA) was used to process TGA data, i.e., to calculate mass loss in % and the onset temperature.

Differential Scanning Calorimetry (DSC)

The DSC experiments were conducted using a Q2000 DSC instrument (TA Instrument, Waters, 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 3–5 mg. Samples were placed in TA aluminum pans and enclosed with Tzero lids. A pin-hole was made in the middle of the lid for each sample prior to loading to the instrument to avoid lids cracking under high temperature. The accurate mass of the samples, empty pans, and lids were calculated. An empty pan with lid was applied for a reference. All samples were subject to heating in the temperature range -30–110 °C at the heating rate of 10 °C/min. The DSC profile was obtained using TA Advantage software (TA Instrument, Waters, USA) and the critical parameters including onset temperature (T_{on}), peak of melting temperature (T_m), and transition enthalpy (ΔH) were analysed by TA Universal Analysis software (TA Instrument, Waters, USA).

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 (TA)

TA penetration tests were performed by adapting ASTM Standard method D1321-9517 using a TA.XT. Plus Texture Analyser (Stable Micro System, UK) using a needle probe with a diameter of 2 mm. The parameters of the experiment were set as follows: 1 mm/s test speed, 5 mm lipstick penetration depth, and 0.5 g trigger force. A sample was placed below the probe in the centre of the base of the instrument. The resistance, expressed as a force in grams detected while the needle probe is penetrating the sample, is the measure of the hardness of the sample. The force as a function of the penetration distance was recorded in Exponent software (Stable Micro System, UK). The hardness of each lipstick was measured at a distance of 3.5 mm and 5 mm, and an average hardness of those was also reported. Hardness was measured for the top and bottom of each lipstick sample.

Oscillatory stress 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 sample was placed in the middle of the serrated platform. The method applied was an isothermal, oscillatory stress sweep at a constant frequency of 1 Hz, and the oscillatory stress was in the range of 10-1500 Pa. 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 the complex modulus (G*) (rigidity) and yield stress (τ) for the linear visco-elastic region (LVR).

Statistical Analysis

In total, 22 lipsticks were used in statistical analysis. The physical characteristics data for hardness and yield stress for all the authentic and other vendors' lipsticks were analysed using descriptive and inferential statistics in SPSS software. Firstly, all the lipsticks were separated into two categories: (1) likely authentic (OR, ST) and (2) likely counterfeit (EB, OB, AE, DH). Notino lipsticks were excluded from the statistical analysis as it was not possible to definitively conclude whether lipsticks were likely to be authentic or not. Secondly, the descriptive statistics provided information on the minimum and maximum (min–max) range for yield stress and hardness as well as the mean and SD. Thirdly, t-test was used to determine if the mean difference between authentic and counterfeit lipsticks was significant.

Results

Sample preparation

A novel and bespoke method for sample preparation was developed. A lipstick cutter (3DCut), Figure 2a, and a rheology guide (3DRheo), Figure 2b, were specifically designed and 3D printed to allow accurate sample preparation and characterisation.

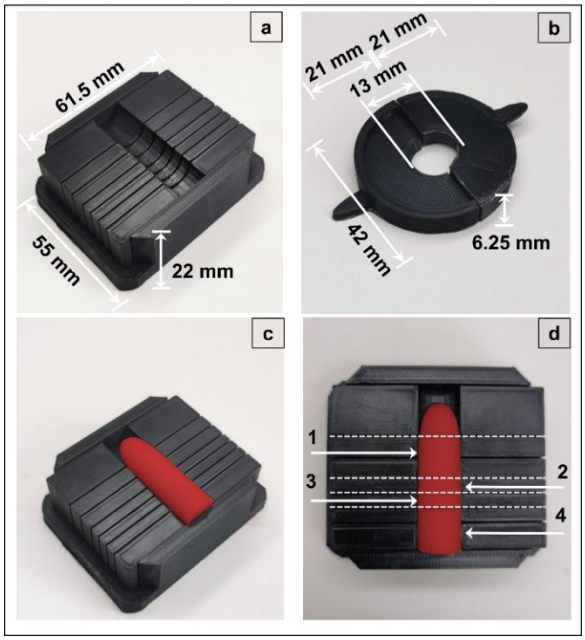

Figure 2. 3DCut **(a)**; 3DRheo **(b)**; Lipstick sample on 3DCut **(c);** Sliced lipstick sample: Element 1–Top texture analysis; Element 2–Rheology; Element 3–FT-IR, DCS, and TGA; Element 4 – Bottom texture analysis **(d)**.

Each sample was prepared for analyses by placing it onto the 3Dcut, Figure 2c, and slicing it with a thin, sharp blade. The 3Dcut had grooves placed at specific distances to determine the thickness of each element of the sample, Figure 2d. Four individual elements formed after slicing a single lipstick sample and each one was used for the following analysis: Element 1– Top texture analysis; Element 2–Rheology; Element 3–FT-IR, DCS, and TGA; Element 4 – Bottom texture analysis.

Fourier Transform Infrared Spectroscopy (FT- IR)

FTIR spectra of beeswax, carnauba wax, and four authentic ST and OR (G01-G04) MAC lipsticks were obtained to identify specific functional groups in the samples, Figure 3a. A high similarity of signal patterns in terms of absorption range and intensity in four authentic lipsticks suggests repeatable results for authentic lipsticks from different sources (online and in-store). Figure 3b represents the FTIR of authentic and counterfeit lipsticks. Analogous multiple peaks can be observed in the 3000-2800 cm^{-1} region among all six samples, in which the maximum absorption signals appear at 2920 cm^{-1}. This can be assigned to C-H stretching vibrations. Additionally, the single peaks (at 1464 cm^{-1}) of different samples assigned for C-H bending vibrations are similar to each other, which proves the presence of aliphatic hydrocarbons with a CH_2 structure in all samples. The medium strength signals at 1740 cm^{-1} related to the C=O stretching suggest the existence of the carbonyl ester group in six lipsticks. In the long wavelength range, the weak bands of genuine lipsticks and carnauba wax in 3720-3600 cm^{-1} with maximum absorption peak around 3690 cm^{-1} belonged to the characteristic signal of OH stretching vibrations.

TGA

TGA is used to characterise lipstick samples by measuring the mass loss as a function of temperature. DSC and TGA are complementary techniques that provide information required for interpretation of the thermal behaviour of the samples. Figure 4a presents TGA plots in specific range of temperature (45-120 °C) for store, original lipstick samples and carnauba wax; and Figure 4b presents TGA plots in the same temperature range for lipstick samples from seven different vendors along with beeswax and carnauba wax. The TGA curves show

a steep drop when temperature is raised above 110 °C, which indicate the onset point of degradation of ST and OR samples. Hence, the range of temperature in DSC experiment is controlled below 110 °C. According to Figure 4a there is no significant mass loss in temperature range 45–110 °C. The average mass loss for ST and OR was 1.237% and 1.061%, respectively. The gentle decline before 110 °C suggests the thermal volatilisation of components, such as moisture or volatile oils. Due to the complexity of lipstick formulation, it is difficult to attribute mass changes in TGA to one specific ingredient. As is shown in Figure 4a, the curve of carnauba wax has a gentle drop at around 90 °C, which corresponds to the melting transition of carnauba wax from DSC analysis [15]. Figure 4a shows that the thermogram of Notino sample resembles the thermograms of authentic samples. According to the TGA profile, a temperature range of -30 to 110 °C was set as the condition for DSC experiment to ensure that the samples did not degrade at high temperatures.

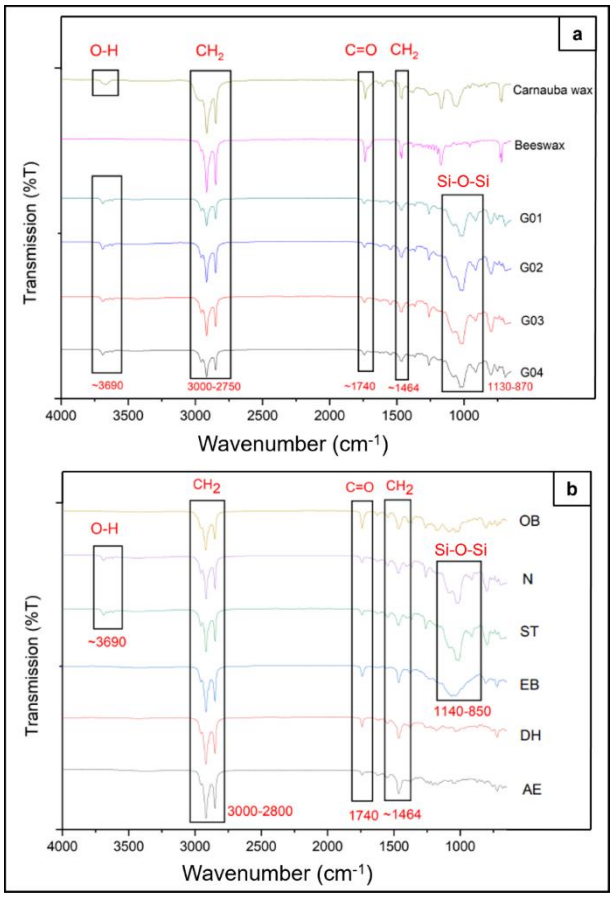

Figure 3. FT-IR spectra. Carnauba wax, beeswax, and four authentic lipsticks **(a)** and six lipstick samples **(b)** with assignment of characteristic absorption bands in rough wavelength range.

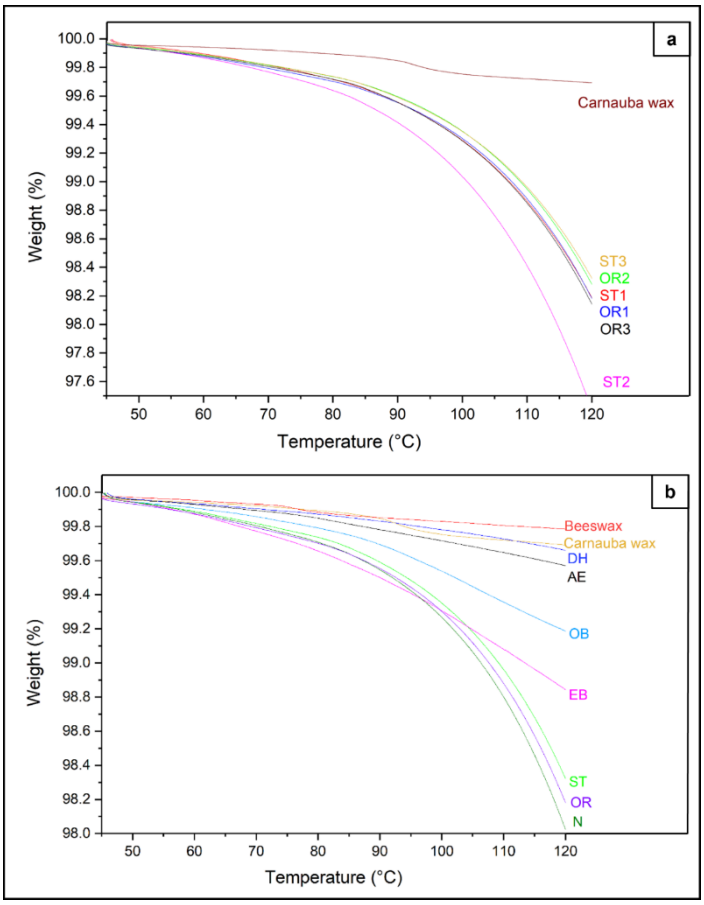

Figure 4. TGA plots in a range of temperature 45–120 ˚C: for store and original lipsticks, and carnauba wax **(a)** and for lipstick samples **(b)**.

DSC

A three-dimensional structure is shaped during the melting and cooling process of lipsticks. The variety of crystal structures of lipstick results in a difference in structural and thermal properties. The physical and morphological characters of wax crystal have been fully analysed with the change of lattice structure [16].

Thermal properties such as melting point have been proven to be affected by the mixture composition of lipsticks [17]. Therefore, the first heating reflects the initial properties and formulation of lipsticks [18, 10].

The DSC profiles provide valuable data of the samples, including the onset temperature (T_{on}), the melting temperature (T_m), and the transition enthalpy (ΔH). The melting peaks in the thermogram are mainly due to the melting of waxes and butters in the lipstick ingredients.

Different types, quantity, and combination of waxes result in various thermal character of lipsticks, which reflect in the difference of melting points and endothermic curve. The transition enthalpy gives an indication of the degree of crystallisation and strength of network inside the lipsticks [10].

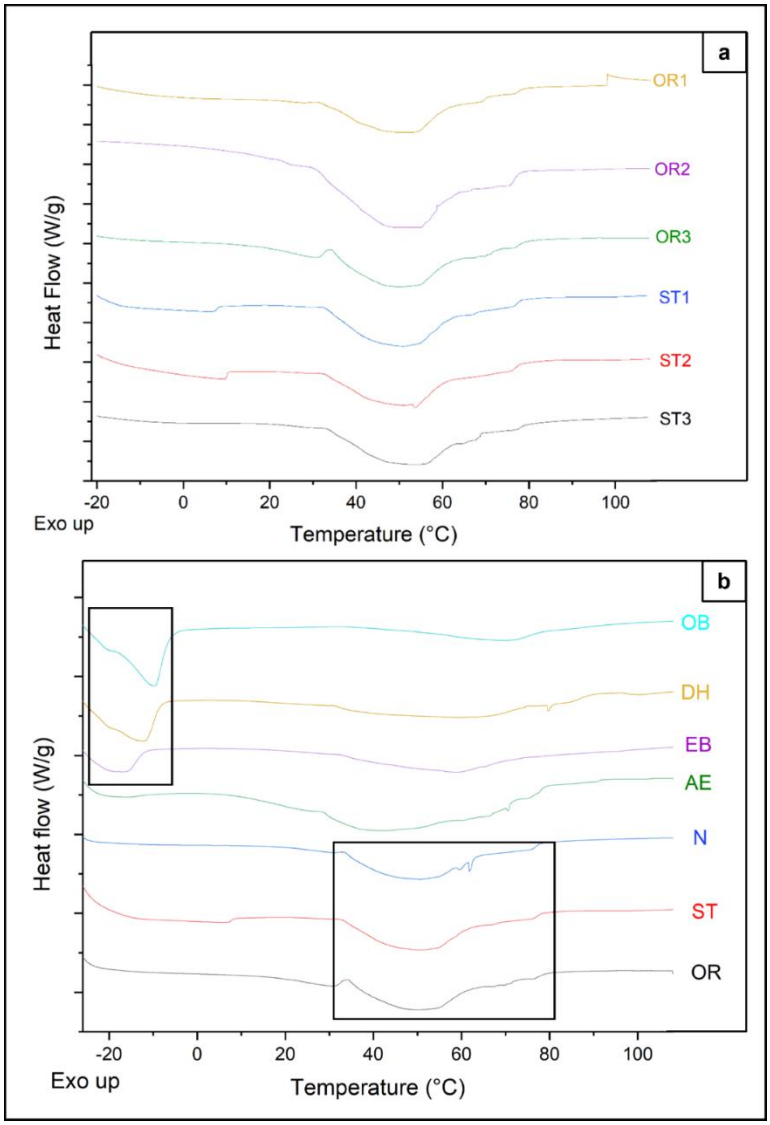

Figure 5. DSC profile of representative samples: six authentic samples **(a)** and seven different vendors **(b)**.

The thermogram in Figure 5a reveals that OR and ST samples have broad endothermic peaks in the range of 30–70 °C with a similar pattern and the maximum melting point around 53 °C, implying that OR and ST have the same formulation. The comparison between thermogram samples from different vendors is exhibited in Figure 5b. OB, DH, and EB have characteristic endothermic peaks in the range of -15 to -5°C, which indicates the presence of moisture or volatile oil. Figure 5b shows that the Notino sample thermogram resembles termograms of authentic samples.

TA

Penetration test provides information on the hardness and the overall homogeneity of the samples. Hardness of samples was measured as the function of the penetration depth. Table 1 summaries lipstick hardness values at 2.5 mm and 5.0 mm for TA lipstick bottom samples and TA lipstick top samples, as well as the average lipstick hardness values. Among all the samples, the hardness of OR and ST rank highest, whereas OB presents the least hardness with the force below 100 g.

Table 1. Lipstick top, bottom, and average hardness (n=10).

	Top hardness (g)			**Bottom hardness (g)**		
Vendor	**2.5 mm**	**5 mm**	**Average**	**2.5 mm**	**5 mm**	**Average**
AE	224 ± 15	234 ± 14	229 ± 6	171 ± 45	166 ± 33	169 ± 3
DH	195 ± 28	214 ± 34	205 ± 14	189 ± 49	161 ± 75	175 ± 20
EB	224 ± 17	239 ± 14	231 ± 11	239 ± 7	235 ± 12	237 ± 2
N	310 ± 35	296 ± 28	303 ± 10	269 ± 19	297 ± 16	283 ± 19
OB	121 ± 11	130 ± 13	126 ± 6	118 ± 11	127 ± 9	123 ± 7
OR	335 ± 52	294 ± 68	315 ± 29	288 ± 29	292 ± 29	290 ± 3
ST	338 ± 9	349 ± 61	344 ± 8	322 ± 19	351 ± 15	336 ± 21

Rheology

Linear Viscoelastic Region (LVR) in oscillatory stress sweep tests is the region with low amplitude stress that indicates non-destruction of the sample [19]. Complex modulus or rigidity (G*) is a measure of the resistance to deformation of the sample. Yield stress (τ) is a useful practical measure of the stress required to induce flow in a product [19]. The length of the LVR is a measure of the stability of the sample and was determined for all rheology profiles as the data point when rigidity drops 10% of its initial value. As shown in Figure 6,

the complex modulus of OR and ST samples resemble each other, which range highest among all samples. The N sample has a slightly lower rigidity than ST and OR, of which plateau value is above 200 kPa. Table 2 shows the average of yield stress and rigidity of samples from different vendors. The similar trend in rheogram of N is consistent with findings in previous experiments, implying that N may have the same formulation as authentic lipsticks. The rigidity of EB and DH are comparable in the range of 150–180 kPa, while DH yields faster than EB. The least rigid samples consisting of AE and OB range from 100–120 kPa. Moreover, the rigidity of OB decreases dramatically with the increase of steer stress, indicating that OB has the lowest yield stress.

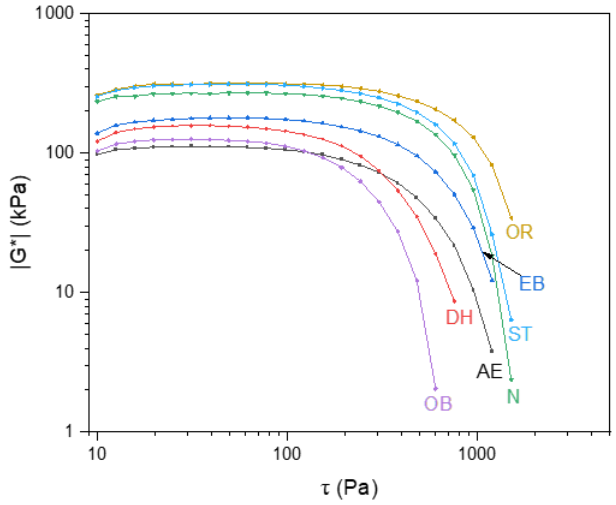

Figure 6. Rheology profiles of the average (top and bottom) rigidity of lipstick samples as a function of oscillation stress.

Table 2. Average of yield stress and rigidity of samples from different vendors.

Vendor	τ (Pa)	|G*| (kPa)
A	126.98 ± 12.40	145.03 ± 12.92
AE	159.00 ± 14.59	102.53 ± 10.33
DH	135.22 ± 13.45	141.14 ± 14.24
EB	210.65 ± 16.70	158.84 ± 15.61
N	229.27 ± 21.96	230.36 ± 15.39
OB	92.41 ± 9.24	119.10 ± 11.94
OR	280.57 ± 20.97	278.47 ± 27.94
ST	245.13 ± 19.84	261.99 ± 24.75

Statistical analysis

The average of four measures of yield stress and hardness (top 2.5 mm, top 5.0 mm, and bottom 2.5 mm and 5.0 mm) were used to analyse the data. This approach was considered best to avoid random error due to the difference in lipstick homogeneity. The results for the descriptive statistics are summarised in Table 3.

Table 3. Descriptive statistics for yield stress and hardness.

Descriptive Statistics						
Aggregated Group		**N**	**Minimum**	**Maximum**	**Mean**	**Std. Deviation**
Authentic mix	Total yield stress	8	216.07	320.86	253.22	34.72
	Total hardness	8	258.78	356.36	325.94	31.61
	Valid N (listwise)	8				
Fake mix	Total yield stress	14	83.41	214.19	138.20	46.92
	Total hardness	14	114.44	246.8	178.24	51.11
	Valid N (listwise)	14				

In addition, the independent samples t-test showed that the difference in yield stress ($t(20)=6.029$, MD=115.018, $p<0.001$, SE=19.08, 95%CI= 75.22466; 154.81210, Cohen's d = 2.7) and hardness ($t(19.774)=8.368$, MD = 147.69, $p<0.001$, SE=17.65, CI 95% = 110.85077 184.53921, Cohen's d =3.3) between the authentic and counterfeit lipsticks was indeed statistically significant. Figure 7 graphically represents the effect size in yield stress between authentic and counterfeit lipsticks.

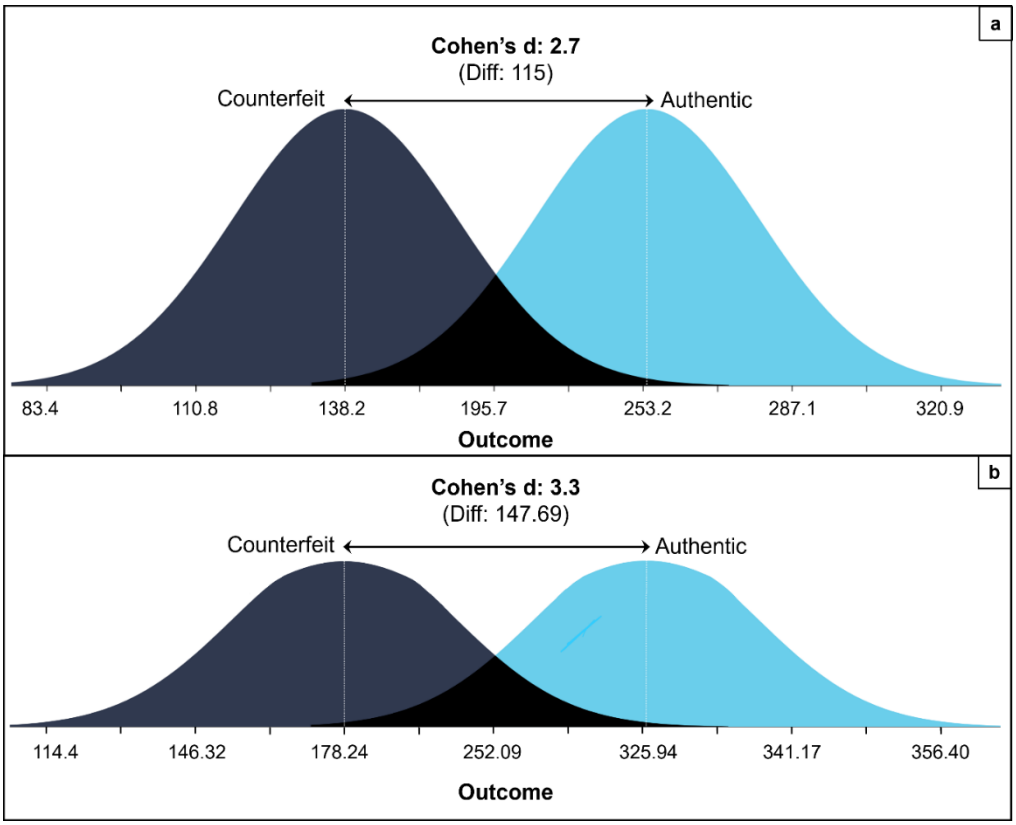

Figure 7. The effect size between authentic and counterfeit lipsticks: yield stress **(a)** and hardness **(b)**.

Discussion

FT-IR results provide a reference to identify counterfeit lipsticks. Authentic lipsticks and carnauba wax show maximum absorption peak around 3690 cm^{-1} (Figure 3) that belongs to the characteristic signal of OH stretching vibrations. This is an indication that authentic lip balms have a substantial amount of carnauba wax. No absorption band around 3690 cm^{-1} is indicative of the absence or not significant quantity of compounds with OH functional group, i.e., carnauba wax. Therefore, samples OB, AE, DH, and EB probably can be recognised as counterfeit. A broad band with intensive absorption shown in EB sample in 1140–850 cm^{-1} corresponds to the Si-O, while it is different from the authentic pattern of multiple peaks in this region. Therefore, the formulation of sample EB may include dimethicone or any other silicone polymer compound with –(-Si-O-Si-)- bond.

TGA curves and mass loss are considered reliable references for the screening of counterfeit lipsticks, which demonstrates the importance in lipsticks differentiation and formula analysis. Figure 4 shows that the TGA thermogram of N presents a high resemblance to the pattern of sample ST and OR with comparable mass loss. This reveals the possibility that sample N is authentic MAC lipstick. Overall, the TGA profiles have revealed a difference of counterfeit lipsticks and authentic ones in thermal property.

The thermal characters can be readily recognised from the DSC profile, which is essential for the differentiation of counterfeit lipsticks. The same formulation can be inferred from the resembling profile. The thermogram in Figure 5 reveals that OR and ST samples have the broad endothermic peaks in the range of 30–70 °C with a similar pattern and the maximum melting point around 53 °C, implying that OR and ST have the same formulation. The result complies with the fact that OR and ST are authentic lipsticks. Since three samples of vendor code are collected from different area of the same DSC lipstick element, the highly identical curves of ST imply the superior of ST in homogeneity than OR. Combining with the TGA profile and FT-IR spectra which imply little moisture exists in the lipstick, other volatile ingredients are assumed to be included in the formulation. Due to the presence of an intense melting peak before 0 °C, as well as a similar broad endothermic peak in 30–80 °C, with the maximum melting temperature of approximately 60 °C, OB, EB, and and DH may contain the same components. The N sample experiences an overlapped melting peak ranging from 33 °C to 80 °C, which resembles OR and ST on the curve. Therefore, the DSC profile of N confirms the results from FT-IR and TGA analysis that N is considered authentic MAC lipstick. Whereas the distinct sharp peak of N at approximately 64 °C which is not visible in OR and ST may be due to batch-to-batch difference. The profile of AE is characterised by an extra broad endothermic peak in the range of 50-80 °C with a melting point 40 °C, which is the lowest among all the samples. The melting point of AE correlated to the sweating character outside the lipstick which was observed during the visual inspection. Furthermore, the broad melting peak with the onset temperature below 32 °C (temperature of lips) may result in partial melting when applying, thereby having a soft texture and good spreadability on the skin. Based on DSC analysis DH, ON, AE, and EB are probably counterfeit lipsticks. Authentic lipsticks bought from different vendors may have slight differences in thermogram

due to the various batches. As such, DSC is not precise enough to determine counterfeits with similar ingredients.

The increasing order of rigidity derived from Table 2 is: OR>ST>N>EB>DH>OB>AE. The least rigid conforms to the lowest melting temperature of AE in DSC profile. While the yield stress order is different form the rigidity, which can be presented in the sequence of OR>ST>N>EB>AE>DH>OB. Hence, the yield stress is independent of rigidity. As soft samples, the yield behaviour varies between samples owing to different formulation of lipsticks or manufacturing procedures. For instance, the AE sample is considered softer in texture but stronger in structure compared with OB and DH. Rheological properties are of great research value for the evaluation of lipsticks since they directly reflect in the softness and ease of application. The similar pattern of yield value and rigidity of OR, ST and N suggests the formulation of authentic lipstick is highly structural stable, which makes deformation less likely when applying. The rigidity of samples is consistent with the results from sensorial analyse, indicating that OR, ST, and N have a relatively hard texture and strong structure. Therefore, the rheological characterisation of lipsticks exhibits rigidity and yield behaviour, thereby supporting the quantitative discrimination of counterfeit lipsticks.

Compared with OR and ST, N has a slightly lower hardness which can be attributed to differences in storage condition or date of manufacture. The comparable hardness of AE, DH, and EB range from 180 to 220 g, which may result in a similar texture when applying. DH and EB experience a resembling fluctuation curve, which implies their possible similarity in ingredients and formulation. The hardness of all samples decreases in the sequence of: ST>OR>N>AE>EB>DH>OB. Since high wax content is a major indicator of the hardness of lipsticks [20], the authentic lipsticks are considered to have a higher proportion of wax. The counterfeit lipstick samples are generally softer than the authentic ones due to differences in formulation and manufacturing process, thereby providing supplementary information for the discrimination of counterfeit lipsticks.

As shown in Tables 1 and 2, the authentic lipsticks had higher yield stress and hardness overall with no overlap between minimum and maximum measures. In addition, the SD was lower for the authentic lipsticks for both measures indicating a similarity of the sample. Any

variation seen between the authentic lipsticks can therefore be attributed to the random measurement error. These results are also consistent with chemical analysis of the in-store and online lipstick.

Figure 7a shows that 97.3% of authentic lipsticks have higher yield stress than the mean of the yield stress for the counterfeit lipstick. However, it also means that 17.7% of the authentic and counterfeit lipsticks will overlap. Figure 7b shows that 99.1% of authentic lipsticks have a higher hardness than the mean of the hardness for the counterfeit lipstick. However, it also means that 9.9% of the authentic and counterfeit lipsticks overlap on their measures of hardness. The results support the hypothesis that parameters (hardness and yield stress) obtained during physical characterisation can be used as an overall reliable substitute for chemical analysis in determining the likelihood of the lipstick to be authentic. The average yield stress of the authentic lipstick should range (95%CI) between 224.2 Pa and 282.2 Pa and the average hardness should range between 299.5 g and 352.4 g.

Conclusion

This study explored the application of physical parameters, yield stress and hardness, for authentication of lipsticks. The authenticity of lipsticks was determined using analytical techniques for chemical characterisation. Statistical analysis supported that yield stress and hardness were accurate predictors of authenticity and showed findings compatible with chemical analysis. The authenticity parameters approach investigated may be used to detect counterfeit lipstick products quickly and reliably.

Acknowledgments. NONE.

Conflict of Interest Statement. NONE.

References

[1] F. Salahioglu and M. Went, "Differentiation of lipsticks by Raman spectroscopy," *Forensic Science International,* vol. 23, no. 1-3, pp. 148-152, 2012.

[2] J. Wong, G. Sauzier and S. Lewis, "Forensic discrimination of lipsticks using visible and attenuated total reflectance infrared spectroscopy," *Forensic Science International,* vol. 298, pp. 88-96, 2019.

[3] A. Bucio, R. Moreno-Tovar, L. Bucio, J. Espinosa-Dávilla and F. Anguebes-Franceschi, "Characterization of Beeswax, Candelilla wax and Paraffin wax for coating cheeses," *Coatings,* vol. 11, no. 3, p. 261, 2021.

[4] Mettler Toledo, "Determination of low concentrations of wax in oils by DSC," 2014. [Online]. Available: https://www.mt.com/dam/non-indexed/po/ana/ta-applications/UC386.pdf.

[5] S. Singh, V. Saran, M. Mishra and A. Gupta, "Forensic examination of lipstick by the various physio-chemical and instrumental method," *International Journal of Social Relevance & Concern,* vol. 3, no. 9, pp. 1-7, 2015.

[6] J. Zhang, H. Jiang, F. Liu and B. Duan, "Differentiation of lipsticks using the shifted excitation Raman difference spectroscopy supported by chemometric methods," in *Optical Spectrocopy and Imaging, and Biomedical Optic*, 2020.

[7] S. Pasieczna-Patkowska and T. Olejnik, "Analysis of cosmetic products using different IR spectroscopy techniques," *Universitaties Universitatis Mariae Curie-Skłodowska,* pp. 95-106, 2014.

[8] M. Gładysz, M. Król and P. Kościelniak, "Differentiation of red lipsticks using the attenuated total reflection technique supported by two chemometric methods," *Forensic Science International,* vol. 280, pp. 130-138, 2017.

[9] V. Sharma, R. Kumar and A. Bharti, "On the spectroscopic investigation of lipstick stains: Forensic trace evidence," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,* vol. 215, pp. 48-57, 2019.

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

[11] PerkinElmer, "Thermal analysis of lipstick utilizing DSC," 2012.

[12] Y. Schuman, "Advanced thermal analysis of phase change materials - Three organic waxes using modulated TGA™ and modulated DSC®," TA Instruments, 2020.

[13] A. Dwivedi, G. Ghosal and P. Belkhode, "Studies in properties of different waxes uUsing DSC and correlating these with the properties obtained by conventional methods," *International Journal of Research in Science and Engineering*, no. March, 2018.

[14] Statista Research Department, "Leading MAC products in Great Britain 2013-2020, by number of users," 26 August 2021. [Online]. Available: https://www.statista.com/statistics/312070/mac-leading-products-in-the-uk/. [Accessed 1 May 2022].

[15] L. Samuditha, K. Dassanayake, D. Kodali, S. Ueno and K. Sato, "Physical properties of Rice Bran Wax in bulk and organogels," *Journal of the American Oil Chemists' Society*, vol. 86, no. 12, pp. 1163-1173, 2009.

[16] B. G. Park and C. S. Ha, "The properties of oil-wax gels with changing lattice structure of wax crystal," *Molecular Crystals and Liquid Crystals*, vol. 569, pp. 143-150, 2012.

[17] A. Bono, H. Mun and M. Rajin, "Effect of various formulation on viscosity and melting point of natural ingredient based lipstick," *Studies in Surface Science and Catalysis*, vol. 159, pp. 693-696, 2006.

[18] J. Rocha, J. Lopes, C. Mascarenhas, D. Arellano, L. Guerreiro and R. da Cunha, "Thermal and rheological properties of organogels formed by sugarcane or candellila wax in soybean oil," *Food Research International*, vol. 50, pp. 318-323, 2013.

[19] Lawson Scientific, "Rheology," Lawson Scientific, 2016.

[20] C. Richard, B. Tillé-Salmon and Y. Mofid, "Contribution to interplay between a delamination test and a sensory analysis of mid-range lipsticks," *International Journal of Cosmetic Science*, vol. 38, pp. 100-108, 2016.