Chapter

Thermal Behavior of Waxes and Its Correlation with Mascara Stability Tests: A DSC Study

Ricardo Alejandro Pineda Beltrán and Johnbrynner García

Abstract

In this work, eight commercial eyelashes mascaras were stored during 15 days at 50°C and a correlation between visually perceived separations over time and the thermal behavior of the waxes present within each product was observed. It was found that 3 of the 8 studied mascaras, displayed noticeable separations which agreed with both changes in their DSC curves and the presence of 2 heat-sensitive waxes in their formula. Finally, it is suggested that the addition of heat-sensitive wax mixtures into a formula should be discarded in order to avoid visual phase-separations and produce thermally stable mascaras that offer the product experience designed for users.

Keywords: cosmetics, differential scanning calorimetry, heat-sensitive materials, mascaras, thermal stability, waxes

1. Introduction

Despite waxes are among the oldest materials known by humans, the word wax covers a wide number of compounds and there is not a generally accepted definition nowadays for that term. According to Krendlinger et al., waxes are substances that are kneadable and not glassy at 20°C, have a drop point >40°C, their melt viscosity does not exceed the 10,000 mPa s at 10°C above the drop point, and usually melt between 50 and 90°C without decomposition [1].

Waxes are extensively used in ceramics, adsorbents, adhesives, paints, medicines and mainly in cosmetics, defining binding and surface properties [1]. Therefore, having a characterization technique for those materials is necessary.

Due to their thermal properties, with the aim of differentiate and identify waxes, Differential Scanning Calorimetry (DSC) is preferred over physical properties or techniques as gas chromatography or infrared spectroscopy [2, 3]. DSC has been also employed in the quantification of wax blends [4] and the thermal stability evaluation after repeated heating cycles [5, 6].

Several studies have found that oil viscosities and wax ratios have great influence on the sensory and mechanical characteristics of cosmetic formulations [7, 8]. Among the skin cosmetics, the ones with a major amount of waxes are lipsticks [9]. Recently, commercially available benchmark lipstick prototypes were characterized using DSC and prototype-dependent fingerprinting was evaluated, mainly in terms of heat stability as well as spreading [10].

Mascaras are products used by 59% of female internet consumers (18+), that make eyelashes appear thicker, longer, darker and with an enhanced curl [11]. Using different techniques among which DSC is reported [12], mascaras are one of the most studied cosmetics since they have some of the highest consumer expectations to meet [11]. As used in lipsticks, a mascara formula contains wax blends to achieve the desired texture [13]; however, to our knowledge, there is not a published research linking the thermal properties of waxes and a key attribute for consumers as the perceived visual appearance [14] (affected by the thermal stability of the product).

The aim of this chapter was to study the relation between the thermal behavior of waxes by means of DSC and the thermal stability screening test of eight commercial mascaras showing the advantages of the continuous development of calorimetry applications in the cosmetic industry focused in efficacy and quality.

2. Materials and methods

2.1 Sample source

The eight commercial eyelashes mascaras were used only for research purposes. Due to the company's policies, the name of each product, the proportions of the individual ingredients in the formula as well as the supplier for each wax are outside the scope of the current study.

The studied waxes were Carnauba wax (Wax-1), Microcrystalline wax (Wax-2), Ozokerite (Wax-3), Paraffin wax (Wax-4), Polyethylene wax (Wax-5) and Synthetic Beeswax (Wax-6).

2.2 Thermal stability screening test

Following a preliminary stability test (also known as screening test), mascara samples were heated at 50°C for 15 days to accelerate the instability processes that could occur, obtaining preliminary information on stable formulations [15]. After 0, 8 and 15 days of thermal stress, each product was carefully observed for phase-separation recording and enough amount of each sample was used to perform DSC measurements. Control samples (day 0) were measured as received from the supplier.

2.3 Differential scanning calorimetry measurements

The DSC curves were obtained using a NETZSCH DSC 204 F1 Phoenix differential scanning calorimeter (NETZSCH-Geratebau GmbH, Selb, Germany) calibrated with Indium, Tin and Bismuth. For each measurement an empty aluminum pan—previously weighted—was used as reference. Mascara and wax samples were weighed (5.5 ± 0.1 mg) and sealed in a 25 μl-aluminum pan and before each analysis, a small hole was opened in the top of the lid. The results were processed using the Proteus software version 7.2.0. The melting temperature (°C), and the transition enthalpy (ΔH, J/g) were estimated.

For waxes a constant rate of 10°C/min in the temperature range of −60 to 180°C was used and three successive heating cycles were recorded under dynamic N_2 atmosphere (20 mL/min) ensuring reliable and reproducible data [10].

Regarding the mascara samples, two heating cycles were used: the first from −20 to 120°C at 10°C/min, and from 0 to 120°C at 5°C/min for the second cycle [16]. All these experiments were made at least by duplicate.

3. Results and discussion

3.1 Wax characteristics

The curves reported on **Figure 1** allow to see the thermal behavior of 6 waxes present within the composition of the mascaras.

DSC curves of waxes 1, 2, 3 and 4 remained unchanged upon followed heating, which can be a stability indicator [17]. On the other hand, DSC curves of waxes 5 (polyethylene wax) and 6 (beeswax) did change.

Although beeswax samples can present DSC differences depending on the origin of the wax [18], they have a single endothermic peak with melting point above 50°C [19, 20] and there are no modifications in the DSC curve after 50 heating cycles [21]. However, the

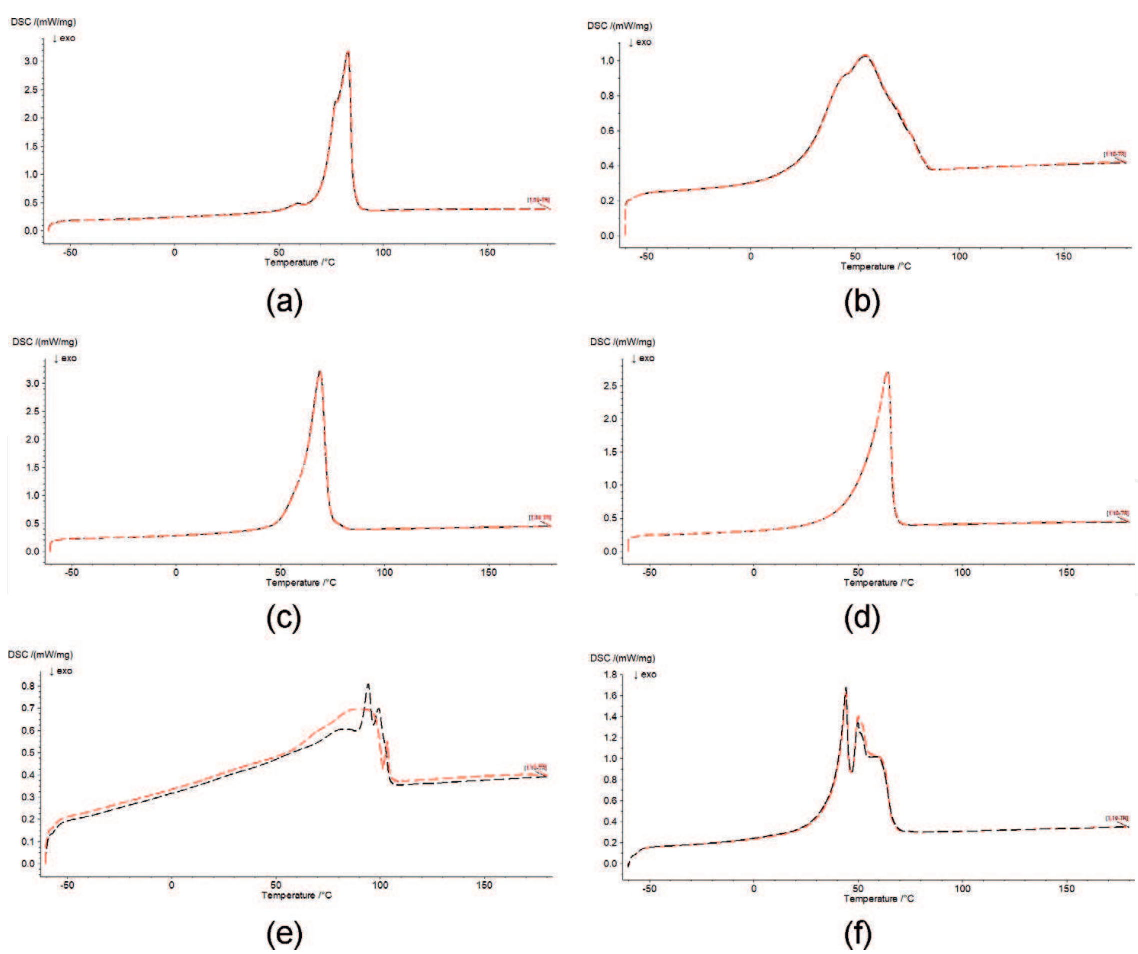

Figure 1.
DSC curves of waxes: Wax-1 (a), Wax-2 (b), Wax-3 (c), Wax-4 (d), Wax-5 (e), Wax-6 (f). In each case the red line (−) and the black line (−) correspond to different heating cycles.

so-called synthetic beeswax (wax-6) sample herein reported is different, since it has two melting endothermic peaks below 50°C and its DSC curve changes between heating cycles.

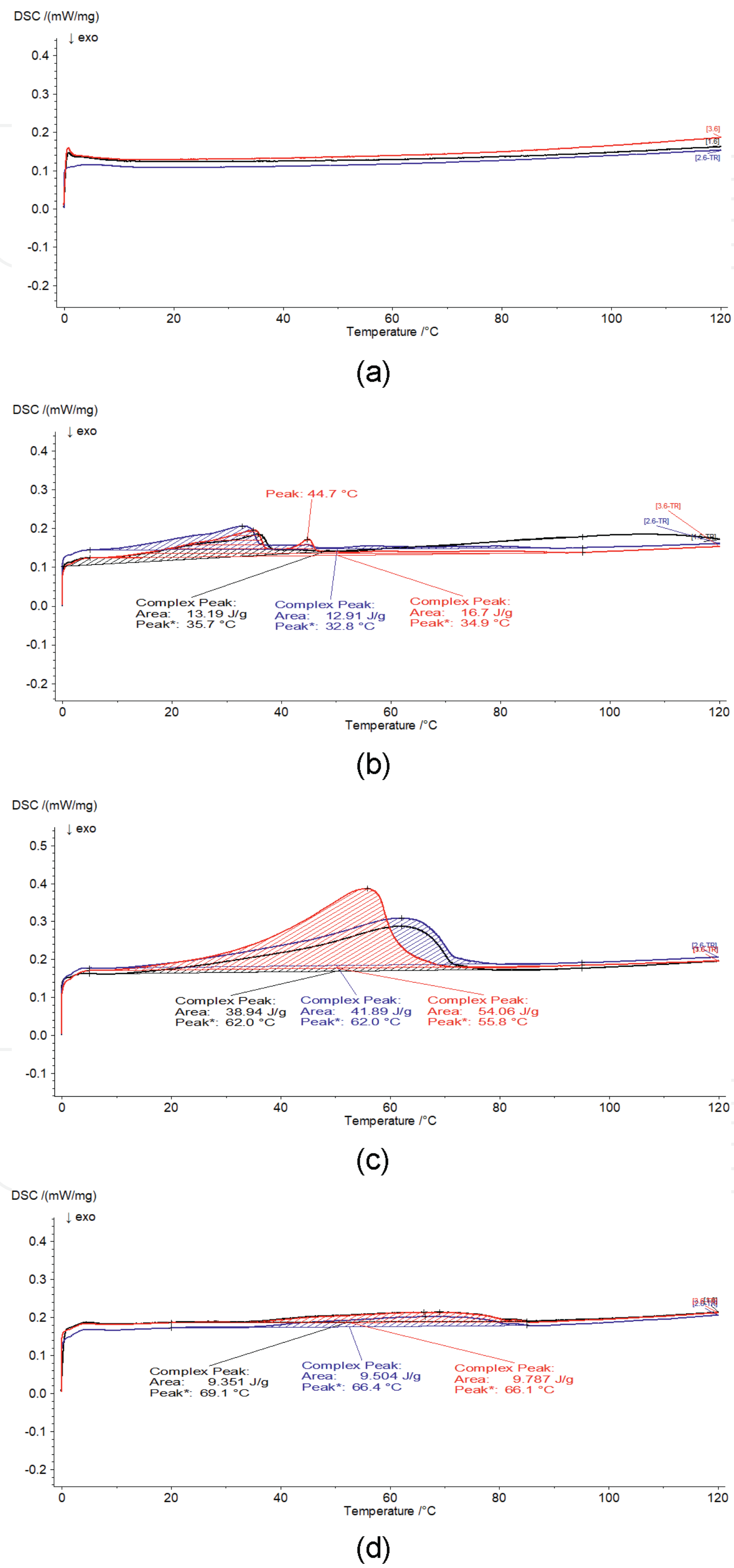

Figure 2
DSC curves of the mascaras M-1 (a), M-2 (b), M-3 (c), M-4 (d). *In each case the black line (–) corresponds to day 0, the blue line (–) to 8 days and the red line (–) to 15 days.*

A change in the thermal behavior of waxes after subsequent remelting cycles is unusual and has been taken as an indicator of variations in the wax structure [22]. For that reason, waxes 5 and 6 were considered as heat-sensitive.

3.2 Correlation with mascaras

Figures 2 and **3** shows the DSC curves for each mascara, while **Table 1** shows the composition of each one in terms of waxes.

Curves without signals (**Figures 2** and **3**) belong to the mascaras that did not have waxes in their composition M-1 and M-8, whereas the mascaras M-2, M-3, M-4, M-5, M-6 and M-7 did show DSC signals in the range between 5 and 95°C and were made of waxes. Also, since mascaras are made of water, pigments, waxes, film formers, emulsifiers, humectants, viscosity agents, preservatives and fibers [11] and waxes

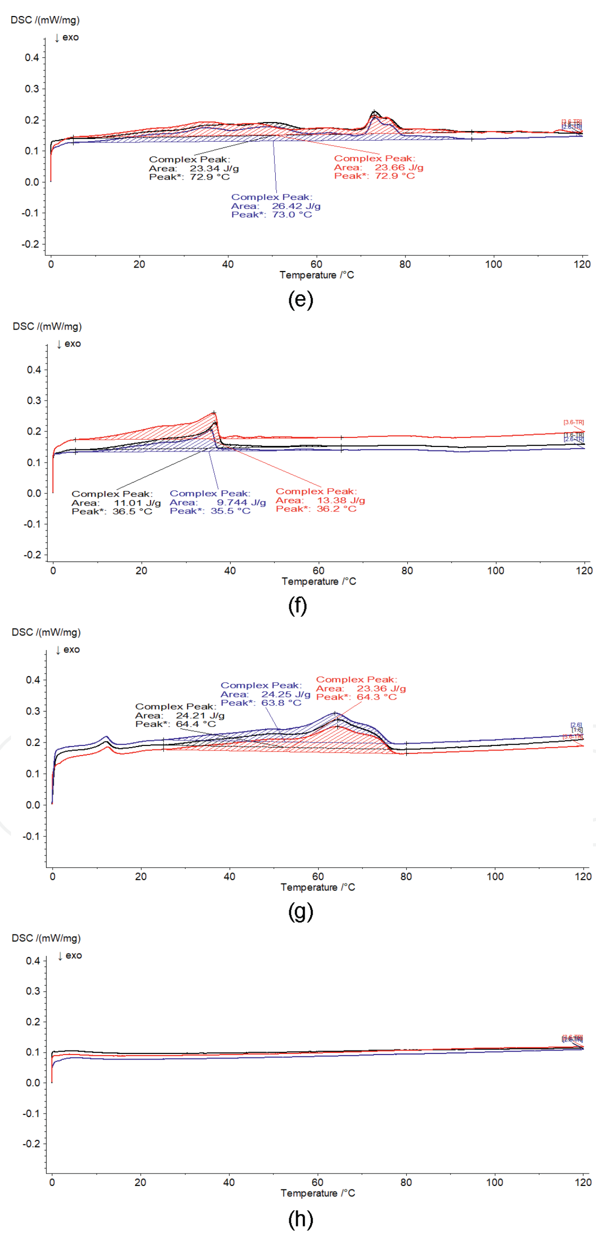

Figure 3.
DSC curves of the mascaras M-5 (e), M-6 (f), M-7 (g) and M-8 (h). In each case the black line (–) corresponds to day 0, the blue line (–) to 8 days and the red line (–) to 15 days.

Wax	M-1	M-2	M-3	M-4	M-5	M-6	M-7	M-8	Heat-sensitive?
Wax-1							X		No
Wax-2			X	X					No
Wax-3			X						No
Wax-4					X		X		No
Wax-5		X	X	X	X	X			Yes
Wax-6		X	X			X	X		Yes

Table 1.
Waxes present in each mascara and their change in DSC curves between heating cycles.

have a melting range between 8 and 100°C [2], the DSC signals are produced by the waxes within the mascara composition.

Although Wax-5 and Wax-6 were labeled as heat-sensitive waxes, mascaras containing one or another (M-4, M-5 and M-7) did not undergo significant changes in their thermal properties in function of time. Likewise, according to **Table 2** (which differentiates the mascaras that presented a noticeable phase-separation from those that did not after being subjected to 50°C for 15 days) M-4, M-5 and M-7 did not show visual separation.

Due to signals on the mascara DSC curve are generated by waxes, it was hypothesized that alterations in the curves of some mascaras could be a consequence of physicochemical changes in the constituent waxes, which is in agreement with evident alterations for mascaras which contained the blend of both heat sensitive waxes (M-2, M-3 and M-6). When comparing the stress at 50°C for 15 days with the other two control times (0 and 8 days at 50°C), an increase in peak enthalpies in more than 20% and separation phenomena were observed. Then, it is possible to say that the mixture of heat-sensitive waxes is one source of incompatibility that yields unstable mascaras.

Given that, it is recommended to check whether the waxes used for mascara manufacture are heat-sensitive. It is necessary to study the specific physicochemical interaction of waxes as well as their ratios, in order to continue the development of meaningful information to predict the stability of mascaras.

Mascara code	Visual changes?	Peak enthalpy variation (%)*
M-1	No	N.A
M-2	Yes	26.6
M-3	Yes	38.8
M-4	No	4.7
M-5	No	1.4
M-6	Yes	21.5
M-7	No	−3.5
M-8	No	N.A

**Respect to day 0.*

Table 2.
Peak enthalpy variation and visual changes after 15 days at 50°C of the analyzed mascaras.

4. Conclusions

Changes in DSC curves of Wax-5 and Wax-6 when applying successive heating cycles were observed, indicating their heat-sensitive nature. Signals between 5 and 95°C on the DSC curve of the studied mascaras are related with the presence of waxes in their composition. Mascaras M-2, M-3 and M-6 displayed changes in their curves after 15 days at 50°C that were related with noticeable phase-separation, such separation could be a consequence of destabilization phenomena after blending at least two heat-sensitive waxes.

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Conflicts of interest

The authors declare that they have no conflict of interest.

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