

Natural oils and waxes: Studies on stick bases

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Synopsis

The objective of the present article was to examine the role of origin and quantity of selected natural oils and waxes in the determination of the thermal properties and hardness of stick bases. The natural oils and waxes selected for the study were sunflower, castor, jojoba, and coconut oils. The selected waxes were yellow beeswax, candelilla wax, and carnauba wax. The hardness of the formulations is a critical parameter from the aspect of their application. Hardness was characterized by the measurement of compression strength along with the softening point, the drop point, and differential scanning calorimetry (DSC). It can be concluded that coconut oil, jojoba oil, and carnauba wax have the greatest influence on the thermal parameters of stick bases.

INTRODUCTION

Oils and waxes are natural products that have been widely used for topical skin application since ancient times. For the last few decades, synthetic substances that can replace natural oils and waxes have become commonly available. However, nowadays there is a rising trend towards the use of natural materials in cosmetology and dermatology (1). Sunflower, castor, coconut, and jojoba oils are the most important oil crops in continental, Mediterranean, and tropical regions. These oils are used for many purposes, including ointments, lotions, sticks, shower gels, and baby care and sun care products (1–6). The candelilla and carnauba waxes originating from tropical areas are more commonly used in lipsticks and decor cosmetics. The most common type of stick is a mixture of waxes and oils that are cast into a solid, elongated form containing dissolved or undissolved active ingredients (7). In order to become more familiar with them and their formulations, it is important to describe and compare their thermoanalytical behaviors (8).

The objective of the present article was to highlight the thermal properties of selected stick compositions prepared from natural oils and waxes. Various examination methods used in the determination of the thermal properties of the prepared sticks were based on pharmaceutical guidelines for the determination of the softening point and the drop point. Furthermore, differential scanning calorimetry (DSC) was applied to examine the role of the quality and quantity of selected oils (sunflower, castor, jojoba, and coconut) and waxes (yellow beeswax, candelilla wax, and carnauba wax). In addition to the components mentioned above, the role of glycerol and lanolin added to formulations was also investigated.

Correlation coefficients between data sets consisting of softening-point measurements, drop point determination, and thermoanalytical parameters measured by DSC are consistent with one another. The hardness of the formulations, a critical parameter from the application aspect, was characterized by the measurement of compression strength.

MATERIALS AND METHODS

MATERIALS

Jjoba oil, castor oil, coconut oil, candelilla wax, and carnauba wax—produced by Henry Lamotte GmbH (Bremen, Germany)—were obtained for research purposes from HSH-Chemie Ltd. (Budapest, Hungary) as a gift. Pharmaceutically pure sunflower oil, yellow beeswax, glycerol, and lanolin were purchased from Hungaropharma Ltd. (Budapest, Hungary).

PRODUCTION OF STICK SAMPLES

The samples were produced by melting the waxes and oils in various ratios. The compositions tested can be found in Table I. The mass of the prepared sticks was 3.0 ± 0.1 g.

DETERMINATION OF PHYSICOCHEMICAL PARAMETERS

Drop point. The drop point is the temperature at which the first drop of the melting substance to be examined falls from a cup under defined conditions. In our study the apparatus used in the pharmaceutical industry was applied. Drop point measurements were carried out according to the method described in the *European Pharmacopoeia Ed. 5.0*, chapter 2.2.17. (9).

Table I
Composition of Samples

Sample (w/w%)	Composition (w/w%)			
	Glycerol	Lanolin	Yellow beeswax	Sunflower oil
1. Sunflower oil (40, 50, 60, 70, or 80)	5	5	50, 40, 30, 20, or 10	0
2. Castor oil (40, 50, 60, 70, or 80)	5	5	50, 40, 30, 20, or 10	0
3. Jjoba oil (40, 50, 60, 70, or 80)	5	5	50, 40, 30, 20, or 10	0
4. Coconut oil (40, 50, 60, 70, or 80)	5	5	50, 40, 30, 20, or 10	0
5. Carnauba wax (0, 1, 2, 3, 4, or 5)	5	5	30, 29, 28, 27, 26, or 25	60
6. Candelilla wax (0, 1, 2, 3, 4, or 5)	5	5	30, 29, 28, 27, 26, or 25	60

Softening point. The softening point, the temperature at which the stick bases soften beyond an arbitrary softness, was determined with the ASTM ring-and-ball method.

Compression strength. The hardness or ability to resist the rupture of sticks (also known as compression strength) was determined by the apparatus used to test suppositories based on fatty excipients. This is described in the *European Pharmacopoeia Ed. 3.0*, chapter 2.9.24. (10).

DSC measurements. DSC thermograms were collected using a thermal analyzer (Haake SII Exstar6000, Seiko Instruments Inc., Neu-Isenburg, Germany). Samples were placed into aluminum pans after which thermal analysis was carried out under the following conditions: samples were heated from 10°C to 150°C at a 10°C/min ramp; likewise, cooling was also performed at a 10°C/min rate. Upon comparison to registered thermograms, the melting point was determined.

RESULTS AND DISCUSSION

Waxes are able to form sticks upon melting without the addition of auxiliary materials. However, their high rigidity is not amenable to comfortable cosmetic or therapeutic applications. For the yellow beeswax used in our study, the softening point and drop point were $64.0 \pm 0.5^\circ\text{C}$ and $63.0 \pm 1.0^\circ\text{C}$, respectively. The compression strength for sticks prepared from yellow beeswax was 5267 ± 44 g. The addition of oil altered the above physical parameters. For a composition of 60 w/w% yellow beeswax and 40 w/w% sunflower oil, the softening point and drop point were $63.5 \pm 0.5^\circ\text{C}$ and $62.0 \pm 0.5^\circ\text{C}$, respectively, while the compression strength was 3734 ± 44 g. The alteration is significant only in terms of compression strength, where the presence of sunflower oil makes the sticks less rigid. It is important to note that the softening point and the drop point are not significantly altered. This is advantageous from the aspect of storage, as the sticks prepared will not be fluid at lower temperatures.

Lanolin has a similar impact on the thermal parameters and rigidity of sticks prepared from yellow beeswax. The addition of 5 w/w% lanolin does not influence the softening and drop points determined for yellow beeswax; however, the compression strength was reduced to 4034 ± 44 g.

The presence of glycerol in higher than 20 w/w% concentrations can lead to phase separation, and therefore the thermal properties measured in this study are characteristic only for the oily components. Thus, in our measurements 5 w/w% glycerol was used throughout the study (Table I.).

The effects of various oils of various concentrations were tested and compared from the aspect of the softening point, drop point, and compression strength of sticks (Table I, Figures 1–3). The presence of oils has a softening effect on the composition of stick bases. However, the extent of the softening effect is dependent not only on the amount of oil, but also on the type of oil (Figure 1). The softening effects can be explained mainly by the different fatty acid compositions (varying chain length and number of double bonds) and, to a lesser extent, by the presence of oil-specific minor components (e.g., vitamin E and carotenoids). It is worth mentioning that the chemical structure of jojoba oil is distinct from that of other vegetable oils. Jojoba oil is a polyunsaturated liquid wax, similar to sperm whale oil, characterized by fatty acids as well as esters composed entirely of straight-chain alcohols. Varying the oil concentrations from 40 w/w% to 80 w/w% results in a measurable reduction of the softening point. The decrease in softening point is

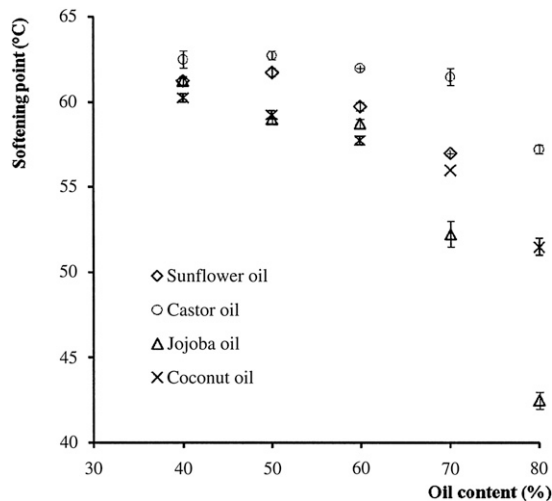


Figure 1. Softening points determined for oily samples composed of 5 w/w% glycerol, 5 w/w% lanolin, and 40–80 w/w% appropriate oil (sunflower, castor, jojoba, or coconut); the rest was yellow beeswax. *n*=3.

less pronounced for castor and sunflower oils, while it is more pronounced for coconut and jojoba oils. In the case of castor oil at concentrations ranging from 40-80 w/w%, the softening point values between $62.5 \pm 0.5^{\circ}\text{C}$ and $57.3 \pm 0.3^{\circ}\text{C}$ can be measured; in the same concentration range, the softening point values for jojoba oil are between $61.3 \pm 0.3^{\circ}\text{C}$ and $42.5 \pm 0.5^{\circ}\text{C}$ (Figure 1). Similarly for the drop point, the presence of oil at higher concentrations leads to lower drop point values. The effect of castor oil concentration on the drop points' changes appears to be the smallest among the oils examined in the present study (Figure 2). In evaluating the hardness of compositions, it can be concluded that between 40 and 60 w/w% oil content, stick bases formulated with castor oil are the hardest,

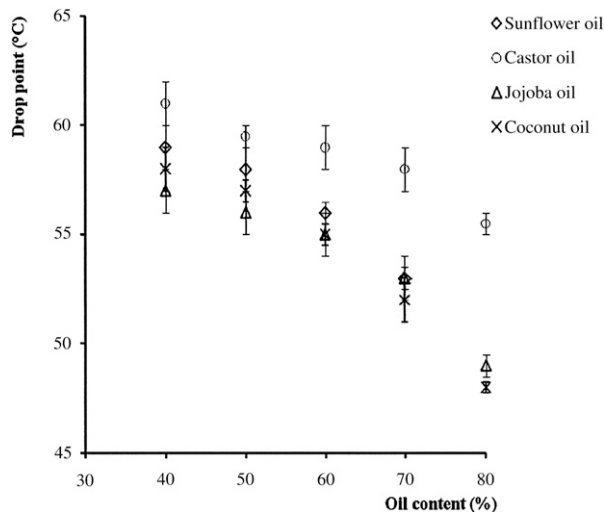


Figure 2. Drop points determined for oily samples composed of 5 w/w% glycerol, 5 w/w% lanolin, and 40–80 w/w% appropriate oil (sunflower, castor, jojoba, or coconut); the rest was yellow beeswax. *n*=3.

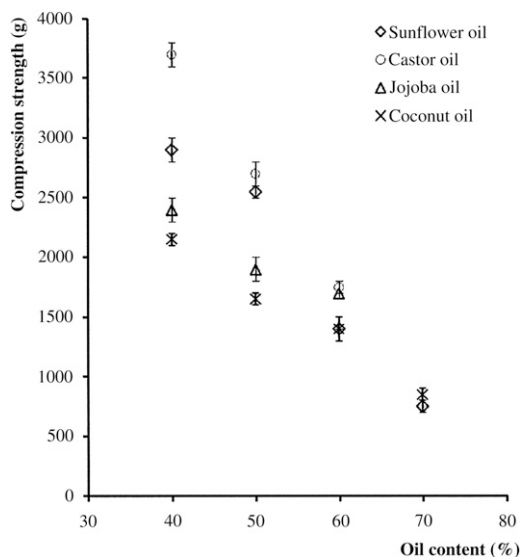


Figure 3. Compression strengths determined for oily samples composed of 5 w/w% glycerol, 5 w/w% lanolin, and 40–80 w/w% appropriate oil (sunflower, castor, jojoba, or coconut); the rest was yellow beeswax. $n=3$.

while sticks prepared with coconut oil are less so (Figure 3). Interestingly, the oils with different origins do not result in different compression strength values in the case of 70 w/w% oil content (Figure 3). It worth noting that for compositions with 80 w/w% oil and above, compression strength cannot be determined due to the soft consistency of the compositions.

On the basis of our organoleptic examination, the taste of castor oil is unpleasant, while better experiences were obtained with jojoba oil. In the case of jojoba oil, the compositions containing relatively high amounts of oil (70–80 w/w%) were too soft and resulted in physically uncomfortable stick application.

The use of waxes in stick compositions most commonly results in improved parameters from the aspect of application. In the present study two waxes were evaluated (Table I, Figures 4–6).

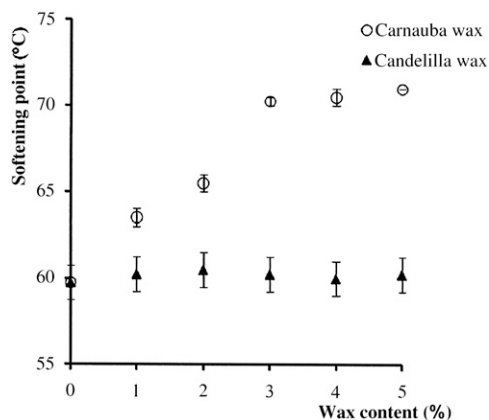


Figure 4. Softening points determined for wax samples composed of 5 w/w% glycerol, 5 w/w% lanolin, 60 w/w% sunflower oil, and 0–5 w/w% appropriate wax (carnauba or candelilla); the rest was yellow beeswax. $n=3$.

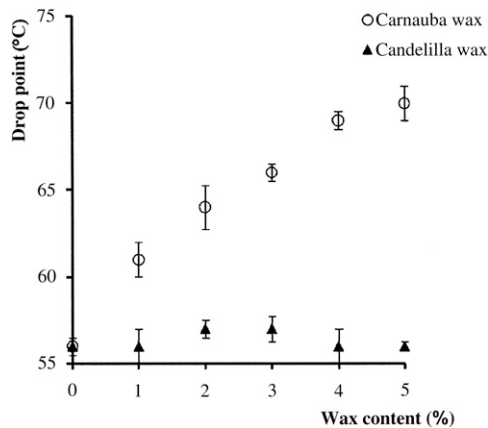


Figure 5. Drop points determined for wax samples composed of 5 w/w% glycerol, 5 w/w% lanolin, 60 w/w% sunflower oil, and 0–5 w/w% appropriate wax (carnauba or candelilla); the rest was yellow beeswax. *n* = 3.

Carnauba and candelilla waxes in concentrations varying between 0 and 5 w/w% were present in the selected compositions, along with yellow beeswax (Figures 4–6). Upon observing the impact of waxes on the softening point, it can be concluded that significant changes were detected only in the case of carnauba wax. For carnauba wax-free samples, the softening point is $59.8 \pm 0.3^{\circ}\text{C}$, while for compositions containing 5 w/w% carnauba wax $71.0 \pm 0.0^{\circ}\text{C}$ is measured. It can be seen that the maximum effect on the softening point can be reached with 3 w/w% carnauba wax content, whereas higher concentrations (4–5 w/w%) do not cause any more change in the softening points. In the case of candelilla wax, the presence and the amount of wax (in a concentration range of 0–5 w/w%) did not seem to influence the softening point (Figure 4). Similarly, the presence of candelilla wax did not seem to have a significant effect on the drop point values of compositions containing 0–5 w/w% wax. In the case of carnauba wax, however, the increasing amounts of wax resulted in higher drop point values, varying between $56.0 \pm 0.5^{\circ}\text{C}$ and $70.0 \pm 1.0^{\circ}\text{C}$ (Figure 5). Also of note, a plateau effect on the drop point can be detected, with a

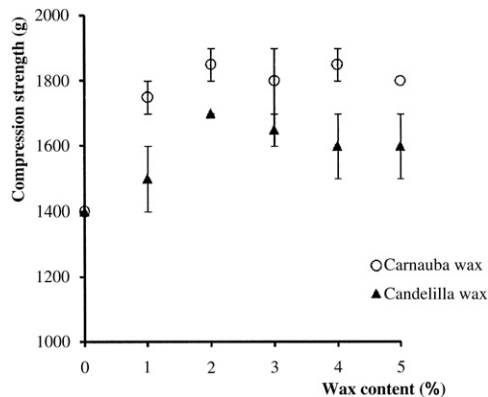


Figure 6. Compression strengths determined for wax samples composed of 5 w/w% glycerol, 5 w/w% lanolin, 60 w/w% sunflower oil, and 0–5 w/w% appropriate wax (carnauba or candelilla); the rest was yellow beeswax. *n* = 3.

maximum drop point achieved at 4 w/w% carnauba wax content, while further increases in the wax content (towards 5 w/w%) do not result in significant drop point changes (Figure 5).

In the case of compression strength measurements, the presence of 1–2 w/w% carnauba or candelilla wax results in a harder consistency. Higher concentrations do not further alter the measured compression strengths (Figure 6).

As DSC is an adequate tool to determine the melting point and phase transition parameters for materials, it was used for the current study (Table II, parts a, b). The results gained by DSC were compared with the softening point and drop point measurements. Furthermore, correlations were examined between the DSC data and the data gained by softening point or drop point determinations. In order to describe the strength of the correlation, the least squares correlation coefficient (R^2) values were calculated and are reported in Table III. On the basis of the R^2 values it is clear that the correlation is strongest between the softening point and the drop point values, with sunflower oil as an outlier. These data allow us to conclude that next to DSC measurements, either the drop point determination or the softening point determination gives more reliable data on the thermal properties

Table IIa
Melting Points (T_m) Determined with DSC for Oily Samples*

Type of oil	Conc. of oil (w/w%)	T_m (°C)
Sunflower oil	40	59.8
	50	58.8
	60	57.2
	70	55.6
	80	55.4
Castor oil	40	62.2
	50	61.1
	60	61.0
	70	58.6
	80	58.8
Jojoba oil	40	62.1
	50	59.5
	60	58.8
	70	57.3
	80	56.3
Coconut oil	40	60.2
	50	60.3
	60	59.9
	70	58.0
	80	54.5

*Composed of 5 w/w% glycerol, 5 w/w% lanolin, and 40–80 w/w% appropriate oil (sunflower, castor, jojoba, or coconut); the rest was yellow beeswax.

Table IIb
Melting Points (T_m) Determined with DSC for Wax Samples *

Type of wax	Conc. of wax (w/w%)	T_m (°C)
Carnauba wax	1	57.1
	2	57.2
	3	60.0
	4	58.4
	5	67.2
Candelilla wax	1	55.9
	2	57.1
	3	56.0
	4	61.0
	5	61.1

*Composed of 5 w/w% glycerol, 5 w/w% lanolin, 60 w/w% sunflower oil, and 0–5 w/w% appropriate wax (carnauba or candelilla); the rest was yellow beeswax.

Table III
Correlation Coefficients Determined for Characterization of the Strength of Correlation between Various Thermal Parameters for Oily and Wax Samples

Sample	Correlating parameters	R^2
1. Sunflower oil	Softening point—Drop point	0.9339
	Drop point—DSC	0.9825
	Softening point—DSC	0.8705
2. Castor oil	Softening point—Drop point	0.8373
	Drop point—DSC	0.7650
	Softening point—DSC	0.4562
3. Jojoba oil	Softening point—Drop point	0.9853
	Drop point—DSC	0.8049
	Softening point—DSC	0.7476
4. Coconut oil	Softening point—Drop point	0.9841
	Drop point—DSC	0.9287
	Softening point—DSC	0.9530
5. Carnauba wax	Softening point—Drop point	0.8760
	Drop point—DSC	0.5098
	Softening point—DSC	0.4300
6. Candelilla wax	Softening point—Drop point	0.4167
	Drop point—DSC	0.3370
	Softening point—DSC	0.2757

of stick formulations than do softening point and drop point determination combined without DSC measurements (Table III).

CONCLUSION

It can be concluded that among the natural oils and waxes studied, coconut oil, jojoba oil, and carnauba wax seem to have the greatest influence on the thermal parameters of the stick bases. Furthermore, upon taking into consideration the softening point and drop point determinations and DSC measurements, strong correlations are observed between the softening point and drop point measurements.

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