Evaluation and Identification of "Snow-White" Material on Lipstick Surface Affected by Synthetic Wax with Stearic Acid and Cooling Time Variation

Habiburrohman, Hafez[1]; Noviani, Widyanita[1]; Rosalia, Purwita[1]; Susanto, Eriwan[1]; **Ramdani, Bayu[1*]**
[1]Research and Development, Paragon Technology and Innovation, Banten, Indonesia.

*Bayu Ahmad Ramdani
Address: Jl. Industri Raya IV, Blok AG No.8, Kawasan Industri Raya Jatake, Tangerang, Banten
Telephone: +6281223333219
bayu.aramdani@paracorpgroup.com

Abstract

Background: Sweating or blooming is one of the undesirable phenomena often occur in lipstick development. It appears like white thick layer or snow crystals on the lipstick surface, which can be affected by many factors including raw material incompatibility to process-related issues such as cooling temperature and time. The purpose of this study was to investigate the effect of lipstick ingredients, especially synthetic wax, and cooling time on this phenomenon.

Methods: Lipstick formulas with different synthetic wax concentrations ranging from 0% to 11% (w/w) were developed. Varies of cooling times were applied from 3 to 9 minutes during the molding process and were also evaluated for the study. The snow-white crystal morphology was evaluated by Keyence VHX-7000 Microscope, Hitachi SU-3500 Scanning Electron Microscope, and Energy Dispersive X-Ray Analysis. The molecular fingerprint of the crystal was determined using fourier-transform infrared spectroscopy.

Results: Among materials in the lipstick formula, we found synthetic wax responsible for "Snow-White" phenomena along with the increment of concentration. Interestingly, we also successfully characterized that the crystal has a high similarity with stearic acid crystal. FTIR results showed a similar functional group with stearic acid. 3 minutes cooling time molding process showed the most severe sweating issue, compared to 6 and 9 minutes cooling time.

Conclusion: our experiment reveals that “Snow-White” sweating phenomena on lipstick surfaces were affected by the quality of synthetic wax which contains stearic acid and cooling time in the molding process where longer cooling time will help to reduce the severity of sweating issue.

Keywords: Lipstick; Sweating; White Crystal; Stearic Acid; Synthetic Wax

Introduction

Lipsticks are intended to enhance the appearance of the lips by adding color and gloss. They are made up of pigments as the colorant as well as base materials like waxes, butter, fats, oils, hydrocarbons, and miscellaneous component. Lipsticks may also contain flavors and fragrances, as well as ingredients for ultraviolet (UV) protection and plumping agent (Baki, 2015). In general, lipsticks formulation consist of 15-25% waxes, 65-80% oils, and 5-10% pigments (Matsuda et al, 2001).

Sweating is a phenomenon caused by temperature fluctuations that causes oil excretion on the surface of a lipstick and is perceived as unattractive by consumers (Seo et al, 1999). The temperature increase modifies the wax lattice and changes the wax/oil equilibrium, causing the oil to migrate from the lattice to the lipstick's surface. It is also suggested that the sweating theory was linked to a poor formula, the better the formula, the higher the percentage of oil that can be included (Dweck, 1987).

According to previous research, several factors influence sweating and blooming phenomenon, including the flaming process, molding temperature, wax and oil compatibility, pigment addition, and ageing (Seo et al, 1999). Unfortunately, the mechanisms underlying sweating and blooming remain unknown (Matsuda et al, 2001).

The experiment tries to substitute candelilla wax with synthetic wax containing stearic acid and investigate the formation of lipstick sweating, then qualitatively identify the snow-white material morphology on the lipstick surface using digital and scanning electron microscope coupling with Energy Dispersive X-Ray Analysis (SEM-EDX); Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (ATR-FT-IR) for their molecular fingerprint; and to evaluate the effect of molding cooling time towards sweating phenomena in lipstick. SEM-EDX and ATR-FT-IR are an example of non-destructive methods to examine lipstick composition (Gładysz et al., 2021).

Materials and Methods

Materials

Neopentyl glycol diheptanoate, polyethylene wax, caprylyl methicone, methicone-coated silica, tocopheryl acetate, phenoxyethanol, titanium dioxide, iron oxide, organic pigment, synthetic wax, and fragrance were obtained from PT Paragon Technology and Innovation.

Preparation of Lipstick Formula in Different Synthetic Wax Concentrations

Several lipstick formula with different synthetic wax concentration: 0%; 0,5%; 1%; 3%; 5%; 7,5%; 11% (w/w) were prepared. It was moulded at –4 ºC for 20 minutes. The prototypes were incubated at 50 ºC in the oven for 1 month. The sweating severity was examined after 1 month storage at room temperature, by visual observation.

White Crystal Morphology Under Keyence Microscope

The snow-white crystal material on the lipstick surface (obtained after 1 month of incubation at 50 ºC) was swabbed and evaluated by using a digital microscope evaluation at 150-1000x magnification.

ATR-FT-IR Analysis

The molecular fingerprint of the lipsticks, stearic acid, and synthetic wax was determined using Attenuated Total Reflection Fourier-Transform Infrared spectroscopy (ATR-FT-IR) (Bruker-Tensor II, frequency range of 4000-500 cm^{-1}, number of scans at 100 s, resolutions 4.0).

White Crystal Morphology Under SEM and EDX Analysis

The snow-white crystal material on the lipstick surface obtained after 1 month of incubation at 50 ºC was swabbed and evaluated by using Scanning Electron Microscope (SEM) (Hitachi SU-3500, Au coated sample) at 1000-15000x magnification. Energy Dispersive X-Ray Analysis (EDX) technology, as one of the additional features in SEM, was also used to evaluate the atomic composition of the sample, we analyzed 8 pointed areas for each EDX image. The digital image obtained under the microscope was compared to synthetic wax and stearic acid raw material's image (including lauric and myristic acid for digital microscope image), to find morphology similarity. EDX spectrum was analyzed to find elemental composition similarity.

Effect of Lipstick Cooling Time on Sweating Severity

Lipsticks containing 1% (w/w) of synthetic wax were prepared by mixing the ingredients followed by molding and cooling at -4 ºC for 3 minutes, 6 minutes, and 9 minutes. After the lipsticks were set up, they were incubated in the 50 ºC oven for 1 month. After that, the lipsticks were stored at room temperature for 2 weeks to evaluate the sweating severity.

Results

Effect of Different Synthetic Wax Concentrations on Sweating Severity

Increment of synthetic wax concentration in lipstick formula is directly proportional to the level of blooming or snow-white effect. The higher concentration of the synthetic wax resulted in a growing number of the white crystal formation on the lipstick surface after incubation at 50 ^{O}C for 1 month (Figure 1).

Figure 1 : Blooming phenomena on lipstick surface. Synthetic wax concentration from left to right in particular order : 0%; 0,5%; 1%; 3%; 5%; 7,5%; 11% (w/w).

White Crystal Morphology Under Keyence Microscope

Differences in normal and blooming lipstick surface can be observed under microscope at 150x magnification as a white crystal layer, the crystals are more obvious to be identified at 200x and 1000x of magnification (Figure 2).

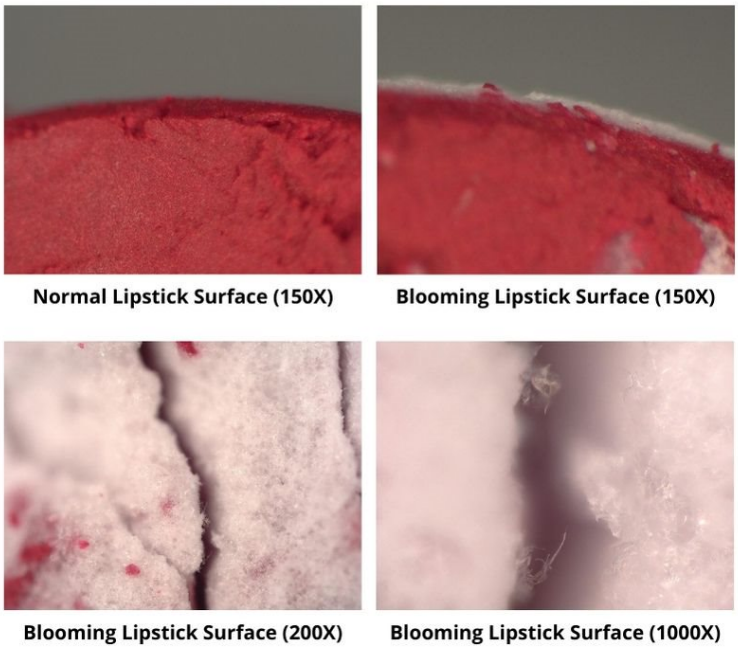


Figure 2 : Blooming phenomena on lipstick surface under Keyence Microscope

White crystal appears on the lipstick surface has similar morphology to pure stearic acid and synthetic wax under microscope observation at 1000X magnification (Figure 3). This result strengthens the hypothesis that the snow-white material is a crystal derived from migrated fatty acid to lipstick surface as a result of sweating and thus crystallized. Of the three morphology of fatty acid observed, stearic acid has the most identical form with the sample and is different from the rod form of lauric acid crystal and needle form of myristic acid crystal.

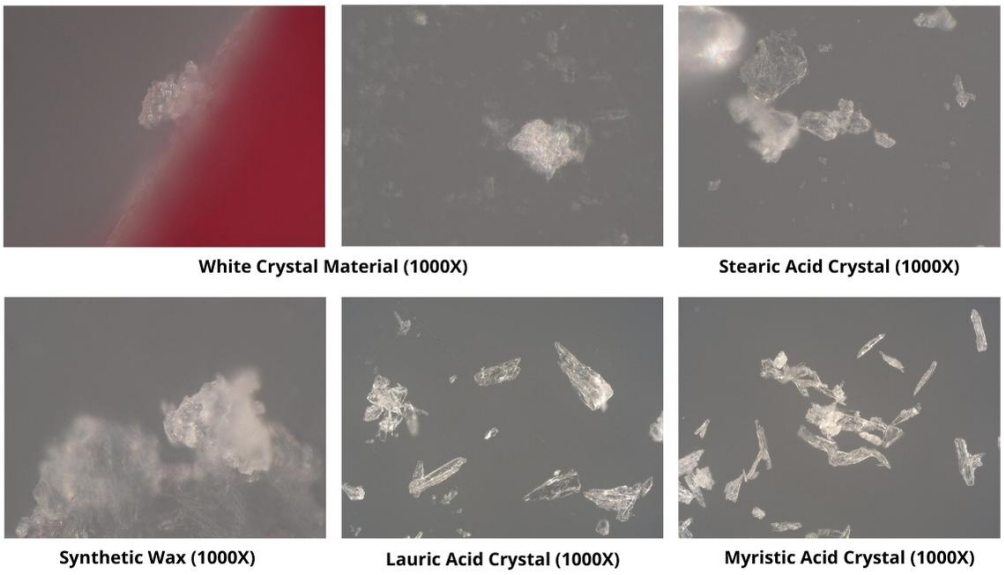
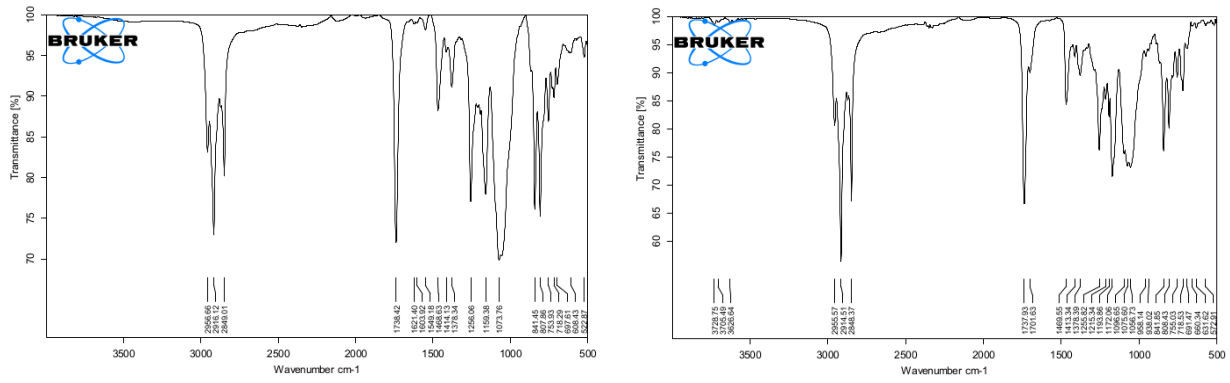


Figure 3 : Morphology comparison between white crystal material with fatty acid crystal and synthetic wax under Keyence Microscope

ATR-FT-IR Analysis

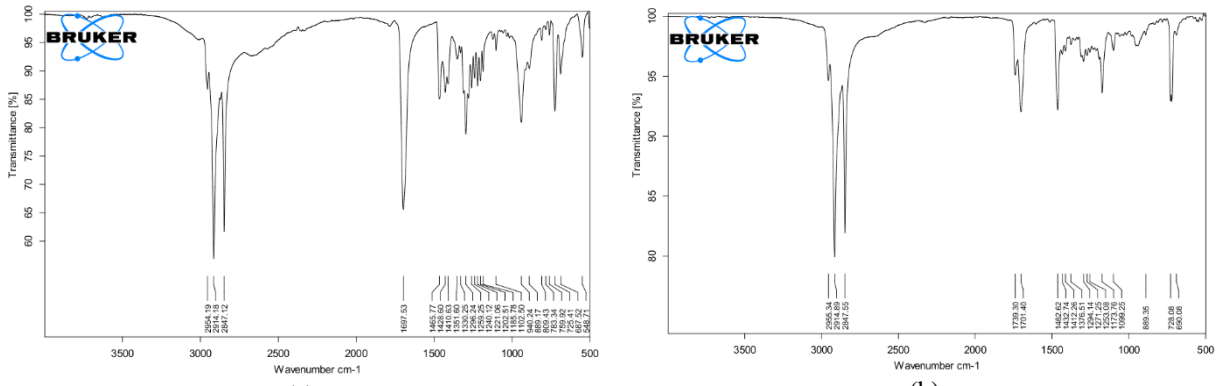
ATR-FT-IR analysis was used to obtain information about functional groups contained in the 4 samples: normal lipstick, blooming lipstick, stearic acid pellets, and synthetic wax pellets. Based on comparison between the normal lipstick spectrum with the blooming one, we predict that there are free O-H stretching groups in the blooming lipstick (3626.64 – 3728.75), and also reduced C-H (1378.39 – 1469.55) and C-O groups (1056.73 – 1255.82) in blooming lipstick compared to normal lipstick (Figure 4).



(a) (b)

Fig 4. IR spectra of normal lipstick (a) and blooming lipstick (b)

Stearic acid and synthetic wax pellets were analyzed by ATR-FT-IR to see their spectra (Figure 5) and compare the four samples (Figure 6).



(a) (b)

Fig 5. IR spectra of stearic acid (a) and synthetic wax (b)

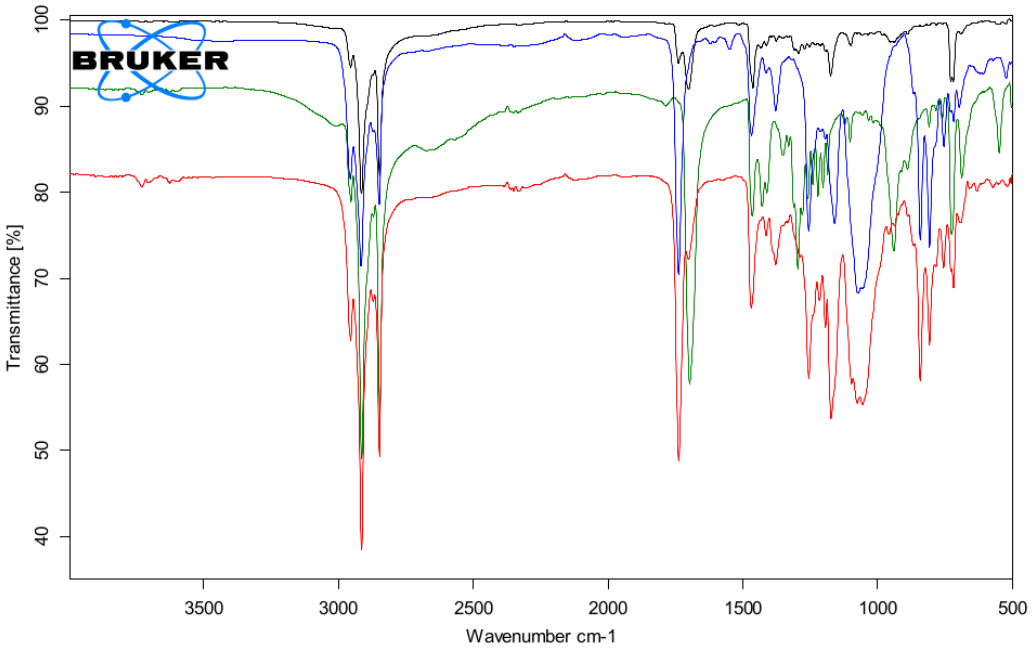


Fig 6. IR spectrum overlay of synthetic wax (black), normal lipstick (blue), stearic acid (green), and blooming lipstick (red)

Blooming lipsticks were heated to generate the blooming effect. Heating may shift IR peaks of lipsticks (Sharma et al., 2019), although further analysis should be conducted to identify the peak shifts precisely.

White Crystal Morphology Under SEM-EDX Analysis

Under electron microscope evaluation, the morphology of snow-white crystal is identical to a synthetic wax, with slightly different from pure stearic acid crystal (Figure 7). Nevertheless, refer to the SEM-EDX spectrum, the percentage ratio of C and O atom of the snow-white crystal is closely identical with the profile of pure stearic acid crystal (Figure 8, Table 1).

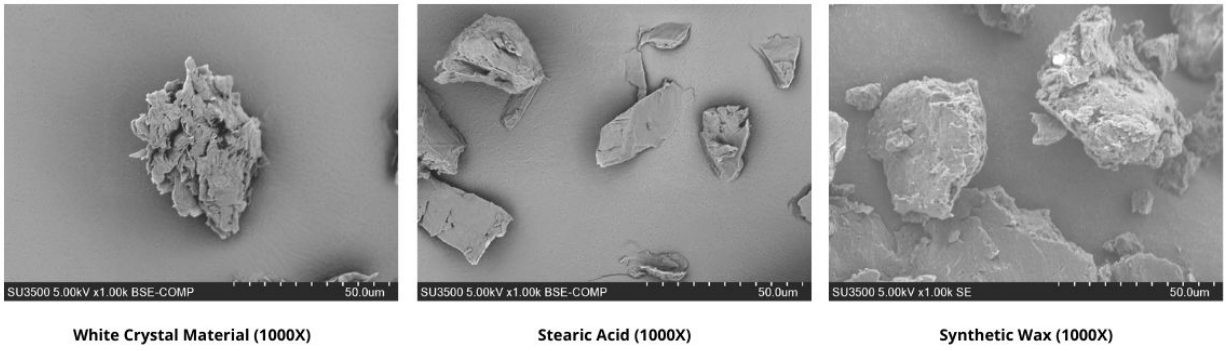


Figure 7 : Morphology comparison between white crystal material with stearic acid and synthetic wax under SEM

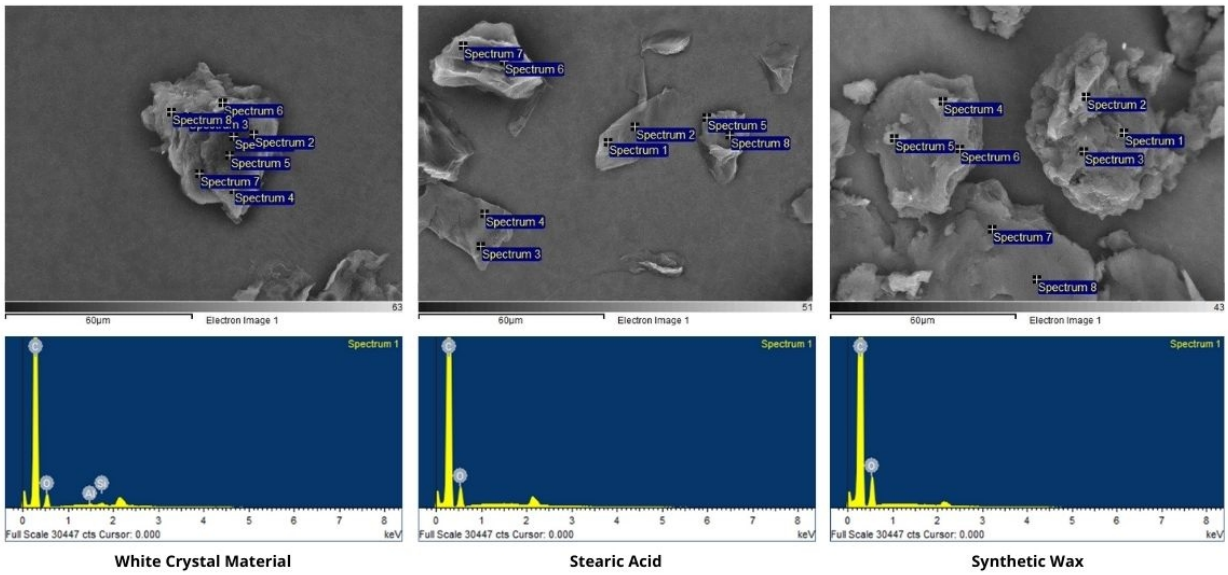


Figure 8 : EDX spectrum comparison between white crystal material with stearic acid

	White Crystal Material				Stearic Acid			
EDX	% Weight		% Atomic		% Weight		% Atomic	
	C	O	C	O	C	O	C	O
Spectrum 1	85.77	13.96	89.00	10.87	87.70	12.30	90.48	9.52
Spectrum 2	88.66	11.05	91.33	8.54	88.67	11.33	91.25	8.75
Spectrum 3	85.35	14.38	88.66	11.22	88.88	11.12	91.41	8.59
Spectrum 4	88.94	10.70	91.57	8.27	86.17	13.83	89.25	10.75
Spectrum 5	88.45	11.30	91.15	8.74	84.22	15.78	87.67	12.33
Spectrum 6	83.95	15.85	87.51	12.40	88.83	11.17	91.37	8.63
Spectrum 7	89.13	10.60	91.69	8.18	83.70	16.30	87.25	12.75
Spectrum 8	86.32	13.49	89.42	10.49	89.02	10.98	91.53	8.47
Sample Average	87.07	12.67	90.04	9.84	87.15	12.85	90.03	9.97
Std. Deviation	1.97	2.00	1.59	1.61	2.18	2.18	1.75	1.75

Table 1 : C-O atom ratio between white crystal material and stearic acid crystal by EDX Analysis

Effect of Lipstick Cooling Time on Sweating Severity

The effect of lipstick molding cooling time at -4 °C has an inverse effect on the severity of the blooming or snow-white effect. After one month of incubation at 50 °C, a shorter cooling time results in numerous white crystal formations on the lipstick surface (Figure 9).

Figure 9 : Cooling time for 3 minutes (left), 6 minutes (middle), and 9 minutes (right)

Discussion

Increased concentration of synthetic wax in a lipstick formula, leads to increased blooming severity occurs. This indicates there is a substance in the wax mixture that is incompatible with the other ingredient of the lipstick formula. The previous study reveals that the breakdown composition of this synthetic wax contains stearic acid (10% (w/w)), which historically has occurred as a root cause of blooming semisolid dosage form. The snow-white material on the lipstick surface was analyzed and confirmed for its identity through several steps of analysis using the advanced instrument.

Morphological analysis by using a digital microscope and SEM reveals that there is a similarity in the structure of the sample with the pure stearic acid. The FTIR analysis also exerts that the sample contains O-H functional group, C-H of Alkana functional group, C-O and C=O functional groups as the same constituent of stearic acid. Nevertheless, the result is yet to be

confirmed as stearic acid, since the above-mentioned functional groups are common groups in organic substances constituents, including another fatty acids, such as lauric and myristic acid.

Comparison of crystal morphology between sample, stearic acid, lauric acid, and myristic acid was further examined. The crystal of lauric acid and myristic acid are observed as rod and needle form crystals, respectively, which is different from the crystal of the sample and stearic acid which is observed as amorphous crystals. Furthermore, the SEM-EDX analysis shows the ratio of molecular weight and atom C-O composition percentage in the sample is identic with the crystal of pure stearic acid. This result becomes strong evidence that snow-white crystal on the surface of the lipstick is a crystal of stearic acid.

Lipsticks were moulded and cooled at -4 °C for 3, 6, and 9 minutes, respectively, to study the effect of cooling time on sweating and blooming. Figure 6 shows that after two weeks at room temperature, the lipstick cooled for 3 minutes was heavily sweated and the lipstick cooled for 6 minutes was slightly sweated. Sweating was very slightly detected in the lipstick after 9 minutes of cooling when compared to the other samples. It was explained that the cooling rate could affect the wax matrix of the lipstick. It was also indicated that as the molding temperature rises, the wax matrix increases as well, reducing the severity of sweating (Seo et al, 1999). We assume that cooling time also influences the wax matrix size of the lipstick.

Conclusion

Stearic acid is a substance that may induce the formation of blooming on the lipstick. The level of blooming severity depends on its concentration in the formula, and the cooling method in the molding process. The experiment results by using a digital microscope, SEM, FTIR, and SEM-EDX analysis, reveal that the snow-white material that appears on the lipstick surface due to the blooming effect is confirmed as stearic acid.

Acknowledgments

This research was fully supported by Paragon Technology and Innovation, and also facilities, scientific and technical support from Advanced Characterization Laboratories Serpong, National Research and Innovation Agency through *E-Layanan Sains Badan Riset dan Inovasi Nasional (BRIN)*.

Conflict of Interest Statement

None

References

Baki G, Alexander K.S, (2015). Introduction to Cosmetic Formulation and Technology. John Wiley & Sons, Inc.; 350. John Wiley & Sons, Inc.; 350

Dweck, A.C. (1981) The sweating of lipsticks. Cosmetics & Toiletries 96, 29–32.

El-Nokaly et al, (1994). Non-Sweating Lipsticks. USA Patent Office. Patent No. 5843407. Dec. 1, 1998.

Gładysz, M., Król, M., & Kościelniak, P. (2021). Current analytical methodologies used for examination of Lipsticks and its traces for forensic purposes. Microchemical Journal, 164, 106002.

Lee, Y.G., Seo, S.Y. and Kang, S.H. (1993) Observation of wax structures in lipstick by Scanning Electron Microscopy. In Proceedings of the 1st ASCS conference,. 222–232.

Matsuda H, Yamaguchi M, Arima H. (2001). Separation and crystallization of oleaginous constituents in cosmetics: sweating and blooming. In Garti N and Sato K (Ed.),

Crystallization Process in Fats and Lipid System, CRC Press, 1st ed., chap. 14. ISBN 9780824705510

S.Y.Seo, I.S.Lee, H.Y.Shin, K.Y.Choi,S.H.Kang and H.J.Ahn (1999) Observation of the sweating in lipstick by scanning electron microscopy. Presented as a poster at the 19th IFSCC conference in Sydney Australia.

Sharma, V., Bharti, A., & Kumar, R. (2019). On the spectroscopic investigation of Lipstick Stains: Forensic trace evidence. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *215*, 48–57. https://doi.org/10.1016/j.saa.2019.02.093