Realization of Low-wax Lipstick by Rubber Molding Technology

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Abstract: Reducing the quantity of wax in lipstick can improve the properties of the lipstick, including the glossiness, moisturizing capability, and longevity. However, lipsticks with less wax tend to break more easily. Therefore, to prevent breakage while reducing the wax content, we focused on the crystal structure of the wax gel and strain generated during the cooling and solidification processes as they are structural factors that affect fragility. Generally, if the crystals and strain are small, the structure is less easily broken. However, because the tip of the lipstick cools more rapidly from below than the root, the strain of the root against the tip increases owing to poor heat transmission. This creates large shrink holes in the root. While reheating from above can suppress the generation of shrink holes, it also causes the crystals to grow larger and the structure to become weak owing to slow cooling. Therefore, we adopted a rubber-molding technology generally used to form logos and complicated shapes as a strategy to mitigate these issues. This successfully reduced the strain generated inside the lipstick during the cooling process, as the rubber mold shrank along with the lipstick, making it possible to quench the root. Therefore, we were able to realize a small crystal structure and low strain on the root of the lipstick. Our results demonstrate that it is possible to realize a lipstick with excellent features by reducing the quantity of wax.

Key words: low-wax lipstick, wax gel, crystals, rapid cooling process, strain, rubber mold

1 Introduction

Stick-shaped products such as lipsticks and stick foundations retain their shape due to the presence of a wax gel with a card house structure, in which liquid oil is contained in wax crystals. Wax gel is formed in the cooling and solidifying process after solid wax is melted, mixed with liquid oil, and poured into a mold (Fig. 1). Lipsticks are shaped by pouring the melted contents into a mold followed by cooling and solidification. The process is the same as that used for chocolates, candles, and soaps. Following this, to form the required shape, the lipstick is generally cooled and solidified along with the mold from the tip part. During the molding process, a mold made of rubber, metal, or resin is filled with the melted ingredients, and the shrink holes generated in the upper center of the lipstick are smoothed by reheating or cutting, followed by the cooling and solidifying of the entire lipstick (Fig. 2).

The metal mold has a high thermal conductivity and cooling efficiency. However, when the container is set in the mold in advance and filled, thermal strain, and thus, breakage can occur because there is a difference between the thermal conductivity of the inner part of the container and that of the mold. Therefore, in many cases, the lipstick is inserted into a container after molding. However, the downside to this approach is that the wax oil gel collapses during insertion and the lipstick does not fit well into the container.

In contrast to that of the metal mold, the thermal conductivity of the resin mold does not differ from the inner part of the container and breakage does not occur easily even if the resin mold is attached to the container in advance and filled from the bottom. Because the wax oil gel solidifies according to the shape of the inner part of the container, the lipstick has a good fit within the container. However, to release the lipstick from the mold, air must enter between the mold and lipstick, which is difficult to achieve using a soft lipstick with a low shrinkage rate.

After the lipstick is solidified by cooling in a rubber mold, the mold inflates and releases the lipstick, so that a logo or complicated shape can be formed. Furthermore, because the mold can be released regardless of the shrinkage of the content, it is possible to mold even soft contents.
with a low shrinkage rate.

With either method, to form the tip of the lipstick, it is necessary to fill the lipstick with the tip facing down, then cool and solidify it from the bottom. Doing this, the tip of the lipstick solidifies first, and the upper center of the lipstick, which is still in a molten state, contracts downward, generating shrink holes.

Thus, because the shrink holes are generated as a result of different degrees of shrinkage resulting from temperature changes between the surface and the interior of the lipstick, this process can be regarded as strain at the upper center with respect to the tip or the side surface. Internal stress is generated while the temperature of the lipstick progresses toward uniformity, which causes sink marks, breakages, or a double core with a hollow interior. Therefore, in general, strain can be eliminated by reheating the upper part\(^4\).

The larger the temperature difference between the surface and the interior, the larger the difference in the degree of shrinkage and the higher the strain. Thus, to reduce the strain, it is important to eliminate differences in temperature between the surface and the interior. When firing ceramics, internal heating using microwaves is known to eliminate the strain caused by uneven temperatures\(^5\).

In addition, during the cooling process, cooling only occurs through heat dissipation. To reduce the strain, it is necessary to slowly cool the entire lipstick or to slowly cool the root by reheating where strain is likely to occur. When strain occurs, the wax structure weakens, but if the wax oil gel is slowly cooled to eliminate strain, the crystal structure of the wax increases in size and still weakens.

However, lowering the wax content in lipsticks is ex-
expected to improve the smoothness, luster, moisturization, and color retention. Therefore, various attempts have been made to strengthen the wax oil gel structure. For example, mixing normal paraffin wax with branched paraffin wax, mixing normal paraffin wax with center-branched wax, bis(polyethylenyl)tetramethyldisiloxane, mixing rice bran wax with botanical High-Melting-Point Alcohol, and mixing candelilla wax with behenyl behenate have all been attempted. Development of these wax compositions has allowed researchers to demonstrate that the hardness of wax oil gel can be increased by reducing the size of the wax crystals in the gel and increasing the contact strength between the wax crystals.

It is also known that the hardness of wax oil gel can be increased by raising the ratio of polar oil and high molecular weight oils. Furthermore, it is known that a wax oil gel composed of amorphous polypropylene and crystalline wax at a specific ratio can control a fine and uniform gel structure and increase the hardness.

However, the above-mentioned problems are difficult to solve, even if the composition is changed. Therefore, we evaluated the molding process, focusing on the relationship between the cooling solidification process, the strain, and internal structure formed during the process. As a result, it was found that the rubber molding technology is an effective molding method.

2 Materials and Methods

A lipstick formulation composed of solid wax and liquid oil was evaluated (Table 1). The coloring agent and powder were removed from the formulation shown in Table 1 for the sample used for SEM (Scanning electron microscope) analysis.

LIPSTICK A was corrected to 100% by diphenylsiloxylphenyltrimethicone, and LIPSTICK B was also corrected to 100% by pentaerythrityltetraethoxanoate.

To observe the crystal formation process with respect to temperature changes, such as the cooling gradient, a polarizing microscope with a cooling and heating device (Pelcher-type cooling and heating stage manufactured by Japan Hi-Tech/OLYMPUS PM20) was used. The wax crystallization process was observed at 76°C, 60°C, and 30°C under the following three cooling gradient conditions: (a) rapid cooling (85 to 75°C in 25 s), (b) slow cooling (85 to 75°C in 10 min), and (c) very slow cooling (85 to 75°C in 42 min).

The crystal shape of the molded product was evaluated by SEM (3D SEM, VE-8800) manufactured by Keyence for contents degreased by ethanol for 24 h.

The lipstick molding conditions used for each observation are as follows.

Molding method A: The slowly cooled molded product was prepared by adjusting the completely melted lipstick to 80°C, transferring it to a mold heated to 65°C, and allowing it to cool at room temperature. The quench-cooled molded product was prepared by transferring molten lipstick adjusted to 80°C to a mold pre-cooled to 0°C and leaving to cool at room temperature.

Molding method B: The lipstick was molded using the resin mold method shown in Fig. 2.

Filling temperature: 82°C, reheat: 265–60°C/4 min, lower cooling: 5°C/2 min, final cooling 5–10°C/4 min.

Molding method C: The lipstick was molded using the

Table 1 Lipstick formula used in the experiment.
rubber mold method shown in Fig. 2.

Filling temperature: 93°C, reheat: 280°C/40 s, lower cooling: 2°C/12 min.

The hardness was measured with a rheometer (manufactured by FUDOH) under the following conditions: 1 mm, 37°C, 2 cm/min, and a 3 mm needle insertion.

A TA Instruments DSC Q1000 was used to measure the crystal precipitation temperature and specific heat. The crystal precipitation temperature was measured at the point where heat generation began to occur when LIP-STICK A was cooled from 110°C to 30°C with a cooling gradient of 3°C/min. The specific heat was measured using the TMDSC (Temperature-Modulated Differential Scanning Calorimetry) method with an average cooling rate of 2°C/min from 100°C to 10°C, a modulation cycle of 100 s, and a modulation amplitude of ±1.0°C.

An Agne thermal conductivity measuring device ARC-TC-1000 was used to measure the thermoelectric conductivity.

The volume change rate and linear expansion coefficient of the wax oil gel (Table 2) were measured using the following procedure.

1. A specific gravity bottle filled with wax oil gel at 95°C, which was completely melted, and squalane at the same temperature, whose temperature-specific gravity was measured in advance, were immersed in a bath heated to 95°C.

2. The temperature of the hot water bath was gradually reduced, and the contracting wax oil gel was supplemented with squalane so that the total volume in the specific gravity bottle remained constant. The volume change rate of the wax oil gel with respect to the initial volume was determined when the volume of the completely melted wax oil gel at 95°C was set to 1 by weight conversion.

3. The relationship between the coefficient of linear expansion (α) and the coefficient of change in volume (β) can be represented by β = 3α when isotropcity is assumed. Therefore, the coefficient of linear expansion of the wax oil gel was calculated using 1/3 of the volume change rate obtained by the above method.

### Table 2

| WAX OIL GEL composition used for volume change rate. |
|-----------------|-----------------|-----------------|
|                 | LIQUID OIL 85%  |                  |
|                 | TRIETHYLHEXANOIN| MINERAL OIL     |
| PARAFFIN        | 13.9            | 1-A             |
| MICROCRYSTALLINE WAX | 1.1          | 1-B             |
| POLYETHYLENE    | 11.1            | 2-A             |
| MICROCRYSTALLINE WAX | 3.9           | 2-B             |
| POLYETHYLENE    | 12.8            | 3-A             |
| MICROCRYSTALLINE WAX | 2.3           | 3-B             |
| SYNTHETIC WAX   | 15.0            | 4-A             |
|                  |                 | 4-B             |

### 3 Results and Discussion

The effect of the cooling gradient in the cooling solidification process was evaluated using method A and LIP-STICK A. We compared the crystal structures of the slow-cooled and rapid-cooled molded products using SEM imaging (Fig. 3). The SEM observations and hardness measurements showed that the rapidly-cooled molded product had a dense wax crystal structure and a large number of

![Fig. 3](image) SEM image of wax oil gel under slow cooling and rapid cooling conditions.
(a) Slow cooled wax oil gel have 0.11 (N) hardness
(b) Rapid cooled wax oil gel have 0.15 (N) hardness
contact points between the crystals, resulting in a high hardness. To decrease the likelihood of breakages, rapid cooling is desirable because it effectively increases the hardness, resulting in a denser crystal structure.

Next, DSC analysis of LIPSTICK A afforded crystal precipitation temperature of 79.8°C. We confirmed the crystal precipitation process using a polarizing microscope equipped with a cooling and heating device. A large number of crystal nuclei were precipitated by quenching the crystal precipitation temperature range (85 to 75°C). Crystals grew from the precipitated crystal nuclei; thus, the size of the crystals was determined by the number of crystal nuclei. Therefore, the more rapidly the crystal precipitation temperature range (85 to 75°C) was lowered, the more the wax crystal nuclei were precipitated and the smaller the wax crystal size became (Fig. 4).

To evaluate the transfer of heat and temperature during cooling and solidification, the thermal conductivity at each molding temperature and the specific heat levels after melting and lowering the temperature were measured for LIPSTICK A (Fig. 5). The results revealed low thermal conductivity and high specific heat within the crystal precipitation temperature range required for reducing the crystal size; thus, when the lipstick is cooled rapidly from the outside, the temperature difference and the degree of shrinkage between the surface and the interior are greater. It is conceivable that this difference occurs due to strain.

Next, using lipstick molding method 2, the crystal structures at the cross sections of the tip, middle, and root of LIPSTICK A, molded using a resin mold (material: HIPS; High Impact Polystyrene), were confirmed by SEM. The hardness of each cross section was then measured and it was confirmed that the crystals at the tips that were rapidly cooled, were small, and had a high degree of hardness, while the crystals at the roots that were slowly cooled by reheating, were large, and had low hardness (Fig. 6).

Next, to clarify the shrinkage characteristics of the lipstick in general, the volume change rate of the wax oil gel was obtained (Table 2), and the linear expansion coefficient was calculated from the volume change rate. In Fig. 7 these linear expansion coefficients are compared with the linear expansion coefficients of the silicone rubber used in rubber molds and the HIPS used in resin molds. The coefficient of linear expansion of the wax oil gel was similar to the coefficient of linear expansion of silicone rubber, while that of HIPS was significantly smaller. Moreover, it can be said that silicone rubber is much softer than HIPS. Therefore, the resin mold cannot follow the cooling shrinkage of the lipstick, but because the silicone rubber is soft and the coefficient of linear expansion is similar, it is thought that the rubber mold is able to follow the shrinkage of the lipstick and shrink along with it. Shrink holes occur when the lipstick solidifies against the inner surface of the mold, and finally, the center of the upper part contracts downward. Because the resin mold is hard and shrinks less than to the
lipstick, the shrink holes become large as they solidify along the inner shape of the mold, but the rubber mold reduces the size of the shrink holes by following the shrinkage of the lipstick. Therefore, for LIPSTICK B, the size of shrink holes produced in the rubber mold and resin mold were compared under the same conditions. The results showed that with the rubber mold, smaller shrink holes were produced. As a result, it was considered that the reheat temperature could be reduced, and LIPSTICK B with the rubber mold could be cooled more rapidly (Fig. 8).

Next, the temperature history of the roots and tips of the resin mold and rubber mold was investigated to find the lowest possible cooling condition that leaves few or no shrinkage holes. The results confirmed that the cooling gradient at the root of the rubber mold was almost the same as that at the tip of the resin mold. Thus, the root of the rubber mold cooled rapidly (Fig. 9).
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For LIPSTICK B, the wax crystal structures at the root of the resin-molded product and the rubber-molded product were compared and evaluated by SEM. The results confirmed that the crystal structure of the root obtained using the rubber mold was smaller and denser than the crystal structure of the root obtained using the resin mold (Fig. 10).

In addition, when the hardness of each part of each cross section was measured, the resin-molded product had a high hardness at the tip and a low hardness at the root, whereas the rubber-molded product had almost uniform hardness and the hardness at the root was higher than both the hardness at the tip and the hardness of the product produced in the resin mold (Fig. 11).

Thus, the rubber-molded product guarantees high quality, and minimal breakage can be expected, even if less wax is used than required for a resin-molded product. Comparisons between eight specialized panels for resin-molded products and rubber-molded products, in which the quantity of wax was as small as possible while still passing quality assurance tests for breakage, demonstrated that rubber-molded products perform better than resin-molded products for smoothness, gloss, moisturizing, and long-lasting color.

4 Conclusion

To obtain a lipstick with excellent features, it is desirable to reduce the wax content, which makes the lipstick soft and easy to break. To strengthen it against breakage, reducing the shrink holes (formed by strain) and creating smaller wax crystals at the root of the lipstick can be effective. By quenching the crystal precipitation temperature range, the wax crystals became smaller. However, the shrink holes became larger because rapid cooling increased the temperature difference between the tip and the root, owing to poor heat transfer. However, if reheating is performed to reduce the shrink holes, the wax crystals at the root become larger and the hardness decreases. To resolve

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**Fig. 9** Temperature history of the tip and root of the resin mold and rubber mold in as lower cooling conditions as possible when there are no shrinkage holes.

**Fig. 10** SEM Image of Crystal structure at the base of the resin mold and rubber mold under quenching conditions with no shrinkage holes.

(a) Resin mold
(b) Rubber mold

**Fig. 11** Hardness for each part under rapid cooling conditions with no shrinkage holes.

(a) 3.0 mm from tip
(b) 10.0 mm from tip
(c) 15.0 mm from tip
(d) root part
these problems, we suppressed the generation of strain (shrink holes) and produced a consistently small crystal size in the root of the lipstick by adopting a rubber-molding technology that shrinks along with the lipstick. The result is a structure that is harder from the tip to the root and is resistant to breakage. The quantity of wax in the lipstick can be reduced with the rubber-molding technology, which delivers lipsticks with excellent tactile quality and durability.

Author Contributions
Hisayoshi Yamashita planned this research, analyzed the data, and wrote the manuscript. Kinya Hosokawa analyzed data. Masami Abe adjusted the lipstick molding conditions. The obtained data were discussed by all members.

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Conflict of Interest Statement
The authors declare that there is no conflict of interest.

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