Enhancement of the Gel Hardness of Candelilla Wax through the Addition of Long-chain Ester Wax Behenyl Behenate

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Abstract: Candelilla wax (CW) is used as an oil-gelling agent in cosmetic sticks. However, its hardness is inadequate compared to those of hydrocarbon waxes such as paraffin. In this study, behenyl behenate (BB), an additive plant-derived wax ester with a high melting point, was shown to improve the oil-gel hardness of CW.

Although the gel with BB alone had a relatively low gel hardness, when BB was mixed with CW at a ratio of 70:30 (CW:BB), the gel hardness significantly increased to four times that of the CW gel. The hardness of the CW and BB mixtures was higher than that of paraffin wax, which is used to solidify cosmetic oils. An increase in gel hardness was not observed when additives with chemical structures similar to those of BB, such as stearyl stearate (which has a lower molecular weight than BB) and behenic acid or behenyl alcohol (which are components of BB), were blended.

Scanning electron microscopy indicated the presence of many spherical clusters comprising fine crystallites in the CW gel. This morphology was in contrast to that of paraffin wax gel, in which only plate crystals were observed. It was concluded that this heterogeneous structure led to the low gel hardness of CW. When BB was added to CW, the spherical clusters disappeared, and the internal structure changed to a homogeneous card-house structure composed of plate crystals.

Key words: oily gel, gel hardness, candelilla wax, long-chain ester wax, behenyl behenate

1 Introduction

Oily gels, which are composed of waxes and various oils, are commonly used in cosmetic sticks such as lipsticks, lip creams, and antiperspirants. The waxes commonly used in these oil-based gels are hydrocarbons derived from petroleum, such as paraffin and polyethylene¹⁻². Gels containing hydrocarbon waxes can be prepared using several types of oils; they do not cause oil separation and exhibit high thermal stability. Hence, they are considered to be ideal oily gels. In recent years, a need has emerged to replace industrial raw materials derived from petroleum resources with plant-derived substances owing to their renewability. Therefore, attempts have been made to fabricate gels using vegetable waxes, such as candelilla wax (CW), carnauba wax, and rice bran wax, or plant-derived materials, such as higher alcohols and long-chain fatty acids, instead of petroleum-derived waxes³⁻¹⁰. However, the gel hardness of plant-derived waxes is typically lower than that of hydrocarbon waxes.

In a previous study, we attempted to improve the gel hardness of rice bran wax by mixing it with various plant-derived additives. The addition of a high-melting-point alcohol (higher than C30) to rice bran wax increased its gel hardness to more than three times that of rice bran wax gel or any higher-alcohol gel¹¹.

However, the obtained gel remained soft, and a hard gel, such as a lipstick made of hydrocarbon wax, was not obtained, potentially because the gel hardness of rice bran wax is the lowest, even among botanical waxes.

Therefore, in this study, we used CW instead of rice bran wax. Among the botanical waxes used in cosmetics, CW has the highest hydrocarbon content. Hence, its properties closely resemble those of hydrocarbon waxes¹²,¹³. Furthermore, the gel hardness of CW is the highest among botanical waxes, and it is used as a gelling agent in food products and cosmetics¹⁴⁻¹⁶, although its gel hardness is still insuffi-
cient for use in lipsticks. This study aimed to develop plant-derived additives for CW (similar to the high-melting-point alcohols for rice bran wax) that can be used to prepare oil gels with hardness comparable to that of hydrocarbon waxes.

2 Experimental

2.1 Materials for gel preparation

CW (MK-4, Nippon Seiro Co., Ltd.) was the plant-derived wax used in this study. Paraffin wax (HNP-9, Nippon Seiro Co., Ltd.) and branched paraffin wax (microcrystalline wax, W-445, SONNEBORN Co., Ltd.) were used as the hydrocarbon waxes for comparison purposes. Behenyl behenate (BB, C_{43}H_{86}COOC_{45}H_{80}) and stearyl stearate (SS, C_{50}H_{102}COOC_{56}H_{118}) were synthesized and employed as long-chain ester waxes. Botanically derived higher fatty acids and higher alcohols were used as the raw materials for the synthesis. For comparison, glyceryl tribenenate was synthesized using identical raw materials. Propanediol dicaprylate/dicaprate (Salacos PR-85, The Nishin Oillio Group, Ltd.), a botanically derived oil, was used as the oil for the gels.

2.2 Preparation of oil gels and gel hardness measurements

Two waxes (CW and BB) in different ratios and oil (10 g in total) were added to a 100 mL glass beaker and stirred at 100°C for 30 min. The wax/oil ratio was 15:85.

The liquid material at 100°C was poured into a polycarbonate cylindrical container with a diameter and height of 3 and 1 cm, respectively, and allowed to stand at 25°C for 24 h. The hardness of the gel in the container was measured using a gel hardness meter (Rheotex SD 700, Sun Scientific Co., Ltd.) equipped with a spherical plunger with a diameter of 5 mm. Three replicates of each sample were prepared, and hardness measurements were performed 7 times for each replicate. The mean and standard deviation calculations were then plotted on a graph.

2.3 Characterization

The crystal structure of the wax inside the gel was observed using scanning electron microscopy (SEM). Prior to observation, oil was removed from the gel using the following procedure. The gel (1 g) was cut out and placed in a 9 mL glass jar, to which 8 mL of ethanol was added and mixed gently. The mixture was allowed to stand at ~25°C for 24 h, after which the supernatant was removed. Thereafter, fresh ethanol was added, and the mixture was gently mixed. This procedure was performed once daily for two weeks. Finally, oil-free samples were dried at 25°C. A thin layer of gold was deposited on the sample, which was then observed using SEM (JSM-6060LV, JEOL Ltd.) at an accelerating voltage of 8 kV.

The crystal structure of the wax gel was observed using optical microscopy. Two drops of the dissolved oil/wax mixture were placed on a glass slide and allowed to stand on a hot plate at 90°C for 1 min. The sample was then cooled for 30 min to 25°C. The obtained thin-film sample was observed using a digital microscope (Keyence VHX-970F) in the polarized mode. The size of the 50 crystals in the image was measured using the attached software, and the average value was calculated.

Wide-angle X-ray scattering patterns of the gels were recorded using an X-ray diffractometer (MX-Labo, MAC Science Co., Ltd.). X-rays (CuKα; λ = 1.54 Å) were radiated at 40 kV and 20 mA. The apparatus was adjusted with a 0.5° divergence slit, 0.5° scatter slit, and 0.15 mm receiving slit. The gel was kneaded, applied to a glass cell, and analyzed in the diffraction angle range of 10°–90° at an acquisition speed of 3°/min at 25°C.

The melting and crystallization temperatures of the samples were measured using a differential scanning calorimeter (DSC-60, Shimadzu Corporation). The temperature was first increased from room temperature to 100°C, then reduced to ~10°C, and finally increased to 100°C. The scanning speed was set to 5°C/min. The melting and crystallization temperatures were determined at the onset of the endothermic and exothermic peaks, respectively.

When the crystallization temperature of the wax could not be distinctly determined using thermal analysis (differential scanning calorimetry, DSC), it was estimated by visual observation. A sample (~0.1 g) was placed on a glass slide and on a cooling stage (Peltier temperature chamber PG-1504, As-one Co.). The cooling rate was set to 1°C/min, and the sample was cooled from 70 to 30°C.

Crystal precipitation was examined by observation using a digital microscope (Dino-Lite Premier M Polarizer, SANKO Co.). The temperature displayed on the cooling-stage device was adopted as the crystallization temperature.

3 Results and Discussion

3.1 Hardness of gels prepared using petroleum-derived hydrocarbon waxes

The hardness of petroleum-derived hydrocarbon wax gels used in cosmetics was first measured to set a target value for the hardness of the botanical wax gel. The hardness and microstructure of the gels were determined using a mixture of n-paraffin (paraffin wax) and branched paraffin (microcrystalline wax) (Figs. 1 and 2).

n-Paraffin formed large plate-shaped crystals in the gel and the microstructure of the wax gel was classified as a coarse card-house structure (Fig. 1). This coarse structure
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led to a low gel hardness (210 g, Fig. 2). By contrast, branched paraffin forms fine, low-crystallinity solids in oils and hence cannot form gels with oils. However, when a small amount of branched paraffin was blended with n-paraffin, the crystal size of the wax within the gel decreased drastically, and a uniformly fine card-house structure was formed. The wax crystals in the mixed system were not simple plate-like crystals but were partially rounded; hence, the crystals were in surface contact resulting in a tougher gel. When n-paraffin and branched paraffin were mixed at a ratio of 80:20, the maximum gel hardness was attained, as shown in Fig. 1.

The following mechanism is responsible for the increase and decrease in gel hardness by blending n-paraffin and branched paraffin. Branched paraffin molecules were adsorbed onto the crystal growth points of n-paraffin, leading to the formation of smaller paraffin crystals. When a small amount of branched paraffin (~80:20) was blended, the n-paraffin crystals became fine and the card-house structure became dense, which increased the gel hardness. By contrast, the addition of higher proportions of branched paraffin leads to a lower gel hardness because branched paraffin, which cannot form gels, becomes the main component of the wax.

The maximum gel hardness (600 g) was set as the target to be achieved by the botanical wax gel. A very fine and uniform wax structure (Fig. 1, right) was required to achieve superior gel hardness.

3.2 Gel hardness of mixtures of CW and BB

Initially, a gel of CW was prepared, and its hardness was measured. Without additives, CW could not form a hard gel with oil, and the gel hardness was 278 g. This value corresponds to those of n-paraffin and branched paraffin gel mixtures at ratios of 100:0 and 40:60 (Fig. 2). The objective of this study was to identify an additive that increases the gel hardness to more than 600 g.

The formation of a uniform card-house structure (SEM image in Fig. 1) is necessary to obtain a favorable gel hardness. Hence, we hypothesized that an additive that readily forms plate-shaped crystals would be suitable. For the additive to affect the crystallization of CW, it was presumed that the precipitation (crystallization) temperature should be similar to that of CW. As an additive with such properties, BB, an ester wax, was selected as the most promising candidate.

Ester wax contained in various vegetable waxes produces plate-shaped crystals. BB is obtained by the esterification of behenyl alcohol with behenic acid; those are the longest alcohol and fatty acid, commercially available. Hence, BB has the highest melting point (68°C) among the practically obtainable ester waxes.

The effects of BB and CW blends were analyzed. As shown in Fig. 3, the gel containing solely CW was soft (278 g). The gel hardness of BB was significantly lower than that of CW (206 g), indicating that BB cannot form a hard gel.

However, when CW and BB were blended at a ratio of...
70:30, the gel hardness drastically increased to 695 g. This value was comparable to the maximum gel hardness obtained using hydrocarbon wax, as shown in Fig. 2.

### 3.3 Microstructure of the gel with CW and BB

To analyze the mechanism of the increase in gel hardness by BB, the microstructure of the gel was observed using SEM. Numerous spherical clusters composed of fine crystallites were observed in the CW gel along with a card-house structure with plate-shaped crystals (Fig. 4A).

The enlarged image of the CW gel (Fig. 4G) indicates that the spherical clusters were composed of small plate-like crystallites. The CW crystallites appeared to grow from the center of the sphere in which the crystal nuclei were present. These spherical clusters were not observed with commercial, purified CW; therefore, we assumed that resin or hydroxy ester, which is removed by purification, may serve as the crystal nuclei. Such spherical clusters were further observed in the rice bran wax gel, in which the gel hardness was low \cite{11}, but not in hydrocarbon waxes, whose gel hardness was significantly higher (Fig. 1). Hence, the presence of such spherical clusters (heterogeneous structures) is assumed to result in a low gel hardness.

Large plate-shaped crystals were observed in the gel prepared exclusively from BB, which was used as an additive in this study (Fig. 4F). Such crystals led to the formation of a coarse card-house structure, which in turn led to a rather low gel hardness similar to that of n-paraffin wax gel.

As the BB-to-CW ratio increased, the size of the crystallites forming spherical clusters increased, and the number of clusters decreased. The clusters finally disappeared and a uniform card-house structure was observed at CW:BB = 30:70 (Fig. 4C). The ratio at which the cluster was not observed was equivalent to the ratio at which the gel hardness was at its maximum. A further increase in the BB ratio led to larger plate-shaped crystals, whose gel hardness is lower than that of the fine structure.

An optical microscopy image of the thin-film gel is shown in Fig. 5. A spherical structure was observed in the CW gel, and coarse plate-like crystals were observed in the BB gel. When these were mixed, fine plate-like crystals that appeared linear in the photograph and the larger ones existed, and a spherical structure was not observed. Although the crystal size and detailed shape were not identical as the cooling conditions were different, these features of the optical microscopic image were consistent with those of the oil-removed SEM observation.

The crystal sizes measured from the optical micrographs are shown in Fig. 6. The addition of 20% CW to BB significantly reduced the crystal size, but the size of these fine crystals was constant at alternative mixing ratios. Spherical structures were observed in the samples with CW:BB = 100:0 and 80:20, and their average sizes were almost identical to those of the fine plate-like crystals.

Thus, the addition of highly crystalline BB at a suitable
ratio eliminated the spherical clusters of CW, leading to an increase in the gel hardness.

### 3.4 Performance of substances analogous to BB as CW additives

Next, we analyzed whether SS (C18·C18), an ester wax with a hydrocarbon chain shorter than that of BB (C22·C22), could improve the gel hardness of CW.

The wax crystals in the SS gel exhibited coarse plate forms, similar to those of BB (Fig. 4F). However, the gel hardness of SS was significantly lower than that of BB, and no increase in the gel hardness was observed when SS was blended with CW (Fig. 7).

The SEM images exhibit that blending SS with CW did not result in the elimination of spherical clusters (Fig. 8B). These results confirmed that SS, whose hydrocarbon chain is shorter than that of BB, cannot be used as an additive for CW.

Table 1 lists the concentration of the oil solutions of the additives (SS or BB) and CW as well as the crystallization temperatures of the solutions determined using DSC. Each wax exhibited a decrease in the crystallization temperature as its concentration decreased, owing to the effect of oil solubility. The temperatures of the 3%–4.5% BB and 12%–10.5% CW solutions were similar. This indicates that in the mixture with BB: CW: oil = 4.5:10.5:85, whose gel hardness was high, the two waxes simultaneously crystallized when cooled.

By contrast, the crystallization temperature of 4.5% SS was lower than that of 10.5% CW by >10°C. The waxes could not crystallize simultaneously when SS and CW were blended at this ratio, hence SS could not increase the gel hardness of CW.

The melting points of the gels with behenic acid, behenyl alcohol (both constituents of BB), and glyceryl tribehenate were almost identical to those of BB (Table 2). Therefore, we investigated whether oily materials with similar melting points have the same effect on CW as on BB (Fig. 9).

Blending these additives with CW did not improve the gel hardness, which is in contrast to that observed in the case of BB. This indicates that having the same melting point as BB is not sufficient for an additive to improve the gel hardness, and that other factors, such as an appropriate molecular shape or length, must be considered.

### 3.5 Characterization of wax crystals in CW- and BB-mixed gels

SEM observations indicated that the spherical cluster...
Fig. 8  SEM images of oil gels with a mixture of CW and SS. CW:SS = (A) 100:0, (B) 80:20, (C) 70:30, (D) 40:60, (E) 20:80, and (F) 0:100.

Table 1  Crystallization temperature of CW and ester waxes at various concentrations in the oil determined by DSC.

<table>
<thead>
<tr>
<th>concentration (%)</th>
<th>Crystallization Temperature (℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>candelilla wax</td>
</tr>
<tr>
<td>3.0</td>
<td>37.2</td>
</tr>
<tr>
<td>4.5</td>
<td>39.0</td>
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<tr>
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<tr>
<td>10.5</td>
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<tr>
<td>12.0</td>
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<tr>
<td>13.5</td>
<td>44.2</td>
</tr>
<tr>
<td>15.0</td>
<td>46.5</td>
</tr>
</tbody>
</table>

Table 2  Melting points of oil gels with various waxes determined using DSC.

<table>
<thead>
<tr>
<th>Waxes</th>
<th>Melting point(℃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Candelilla wax</td>
<td>51</td>
</tr>
<tr>
<td>Behenyl behenate</td>
<td>68</td>
</tr>
<tr>
<td>Stearyl stearate</td>
<td>58</td>
</tr>
<tr>
<td>Behenic acid</td>
<td>78</td>
</tr>
<tr>
<td>Behenyl alcohol</td>
<td>63</td>
</tr>
<tr>
<td>Glyceryl tribehenate</td>
<td>63</td>
</tr>
</tbody>
</table>
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composed of wax crystals disappeared, and the crystals changed to a uniform plate shape by blending with BB (BB:CW = 30:70). This significant change might be caused by a variation in the crystal system, similar to the triglyceride crystals in chocolates. X-ray diffraction measurements of the gel were conducted to verify whether the blending of BB and CW leads to the change in the crystal system of the wax (Fig. 10).

Two peaks were observed at d = 0.38 and 0.41 nm in the CW and BB gels, representing a typical orthorhombic crystal pattern. Although their crystal shape and size in the gels appeared to be very different, they were in identical crystal systems.

The peak patterns or peak positions (lattice spacing) were constant, irrespective of the mixing ratio of CW and BB in the gel. Therefore, blending CW and BB did not create a unique crystal system which may affect the gel hardness or the wax crystal shape.

3.6 Precipitation behavior of coexisting CW and BB melt

The interaction between the two wax molecules was considered the next potential mechanism that could explain the variation in the crystal shapes. For example, if the two types of wax molecules form a solid solution or eutectic, the shape of the crystals changes significantly. In this case, eutectic crystallization, in which two types of waxes simultaneously form uniform microcrystallites, is highly probable. The formation of eutectics by CW and BB can be confirmed using a phase diagram based on the crystallization temperature.

Initially, we attempted to measure the crystal temperature using DSC, but the two exothermal peaks intermittently overlapped. Therefore, the precipitation behavior during the cooling stages was observed using an optical microscope.

Pure BB or CW crystallized in one step during cooling to 40°C; the former formed yellowish crystals, while the latter formed large translucent crystals. The mixture of BB and CW exhibited two-step crystal precipitation. First, yellowish crystals (BB:CW < 20:80) or translucent coarse crystals (BB:CW > 50:50) were formed in the liquid phase. The former appeared to be pure CW crystals, while the latter was BB, based on its appearance. During cooling after the first precipitation, the crystals gradually grew, following which the second precipitation of fine crystals suddenly occurred at ~59°C. At this step, the sample turned white. The phase diagram, obtained from the temperatures at which precipitation began, is shown in Fig. 11.

Although the first (higher) temperature varied with the

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**Fig. 9** Hardness of gels with mixtures of CW and various waxes.
○: glyceryl tribehenate △: behenyl alcohol □: behenic acid.

**Fig. 10** X-ray diffraction patterns of oil gels with a mixture of CW and BB.

**Fig. 11** Phase diagram of the mixture of CW and BB.
●: Yellow small precipitate; ○: translucent coarse precipitate; ■ White fine precipitate.
mixture ratio in the range of 69–78°C, the lower temperature remained constant at \( \sim 59^\circ C \), irrespective of the ratio. The crystallization temperature lines converged to one at a CW:BB ratio of 70:30. This phase diagram is typical when eutectics are formed, and similar examples are reported with mixtures of various natural waxes or those of long-chain fatty acids and alcohols\(^{18-22}\).

The first (higher) temperature corresponded to the precipitation temperatures of either BB or CW, and the second temperature corresponded to the eutectic temperatures of BB and CW. The eutectic composition BB: CW = 30:70 is the composition at which the gel hardness was at its maximum.

From these results, we propose a mechanism in which CW and BB form eutectic crystals (fine uniform crystals) at a ratio of 70:30, respectively. The fine card-house structure composed of these crystals enabled the attainment of the highest gel hardness at this ratio.

### 4 Conclusion

To improve the oil-gel hardness of CW, we used a long-chain ester, BB, which was synthesized by the esterification of plant-derived longest-chain alcohols and fatty acids. Although the BB gel had a relatively low hardness, when it was mixed with CW at a ratio of 70:30 (CW:BB), the gel hardness improved and surpassed those of widely used hydrocarbon waxes. The use of materials similar to BB, such as SS, behenyl alcohol, and glyceryl tribehenate, did not improve the gel hardness.

The SEM images showed numerous spherical clusters comprising fine crystallites in the CW gel. This heterogeneous structure presumably led to the low gel hardness of the CW. When BB was mixed with CW, these spherical clusters disappeared, and a homogeneous card-house structure composed of plate crystals was observed. It was considered that the change in the microstructure of the gel caused by BB increased the gel hardness.

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### References


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