CONTROL OF HARDNESS OF OIL-WAX GELS BY A NOVEL BRANCHED WAX AND APPLICATION TO LIPSTICKS

K. Yoshida [1], M. Shibata [1], Y. Ito [2], G. Nakamura [2], H. Hosokawa [1]

[1] Kao Corporation, Skin Care Products Research Labs., 2-1-3, Bunka, Sumida, 131-8501 Japan

[2] Kao Corporation, Material Science Research Labs., 1334, Minato, Wakayama, 640-8580 Japan

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Summary

A novel branched wax has been developed for the control of the hardness of oil-wax gels. Using this wax, glossier application and smoother texture but tough lipstick can be obtained.

Oil-wax gels are oily solids composed of liquid and crystalline solid oils (waxes). They are widely used in various cosmetic products, especially lipsticks. The control of gel hardness is one of the most important techniques in improvement of the lipstick quality.

Addition of small amounts of commercial branched paraffin wax (e.g. microcrystalline wax, b-PW) to n-paraffin wax (n-PW) has been commonly used to increase gel hardness. However, gel hardness is very sensitive to the quantity of b-PW and the gel obtained is not always hard enough for practical use.

In this study we examined the relationship between the gel hardness and the properties of the wax crystal in the gel. We have found that, when b-PW is added to n-PW, the wax crystal size becomes smaller (hardening the gels) and its crystallinity is decreased (softening the gels) simultaneously.

Considering this result, we have developed a novel branched wax, Bis(polyethylenyl)-tetramethyldisiloxane (named ESE). ESE molecules are composed of a central tetramethyldisiloxane unit (branch unit) with polyethylene units at both ends. The central unit may suppress crystal growth while the ends are expected to prevent a decrease in wax crystallinity during crystallization. When ESE is added to n-PW, the wax crystal obtained becomes smaller without decreasing in crystallinity; consequently, the gel hardness is dramatically increased.

By using ESE, the total amount of wax in a lipstick can be decreased by 30% without spoiling the stick toughness, thereby achieving glossy application and smooth texture.

1. Introduction

Oil-wax gels are oily solids containing both liquid oils and crystalline solid oils (waxes). Their use is widespread in various cosmetic products, especially lipsticks. The control of the gel hardness is one of the most important techniques for the improvement of lipstick quality.
In an oil-wax gel, an assembly of plate-like crystals forms a three-dimensional structure with liquid oil contained in the cavities constructed by the crystal plates [1].
The number of connecting points to each wax crystal and the connecting strength between crystals determine the gel hardness [2]. It is known that variation of gel hardness depends particularly on the polarity of the oil [3].
In a previous report, we have studied the internal structure of the gel and the mechanisms of formation underlying its hardness using gels composed of n-paraffin wax (n-PW) and various polarity oils. The variation of gel hardness was found to be related to the surface roughness of the wax crystals. Rougher surfaces mesh with each other more tightly, and consequently the three-dimensional structure in the gel consisting of the wax crystals becomes more rigid [1].
In cosmetic use, such as in lipstick, it is necessary to use oils that are good for pigment dispersibility. Thus, for the control of the hardness of the oil-wax gel, there is higher practical value in improving the properties of the wax rather than of the oil.
Among the methods for gel hardness control by waxes, adding a small amount of commercial branched paraffin wax (b-PW) to n-PW has been the most widely used. However, the gel hardness is very sensitive to the quantity of b-PW and the gel obtained is not always hard enough for practical use.
In this study, we first investigated the relationship between gel hardness and the properties of the wax crystals present when n-PW and b-PW are mixed together. Then, based on this result, we have developed a new branched wax; the characteristics of this and its applications to a lipstick were also examined.

2. Experimental

2-1. Oil and wax samples

Waxes: n-paraffin wax (n-PW: Solid paraffin), commercial branched paraffin wax (b-PW: isoparaffin, C_{31}-C_{70} hydrocarbons, 63-93°C melting point). Bis(polyethylenyl)-tetramethyldisiloxane (ESE). The synthesis of ESE is shown in Scheme I. Ethylene was polymerized with n-butyllithium as the initiator in the presence of tetramethylethylenediamine (TMEDA), then terminated with D5 and dehydrated to obtain ESE [4].
Oil: Neopentyl Glycol Dicaprate

2-2. Preparation of oil-wax gels

The appropriate amounts of oils and waxes were heated at 100°C and stirred to form a homogeneous solution. The mixture was poured into a stainless steel dish and allowed to stand at room temperature for over 12 h.

2-3. Measurements of the oil-wax gel properties

The gel hardness was measured on a Rheometer (RHEOTEC Co., NRM-2010J-CW) at 20°C by inserting the cylindrical plunger (2 mm in diameter) into the gel.

The crystallinity of the wax in the gel was estimated as the peak intensity of d(110) against the maximum of the amorphous halo ($I_{(110)}/I_{(Amorph.)}$) measured using a PHILIPS PM1700 X-ray diffractometer (XRD) [5].

The crystal size was estimated by SEM imaging. To remove the oil, the oil-wax gel was washed in acetone overnight and then dried at room temperature for over 12 h. The structure of the obtained 'oil-free gel' was observed by using a JEOL JSM6330F scanning electron microscope (SEM).

2-4. Analysis of the internal structures of wax crystals

Waxes were dissolved in 1% n-hexane at 50°C. This suspension was dropped on the glass and crystallized by drying at room temperature. The vertical ultrathin sections of dried wax crystals were stained with RuO_4 and observed by using transmission electron microscopy (TEM, HITACI H-7100FA).

The interplanar spacing of the wax crystals was estimated by XRD (PHILIPS PM1700).

2-5. Preparation and evaluation of model lipsticks

The ingredients shown in Table I were heated at 90°C, uniformly blended, poured into a mold and then cooled to prepare the lipsticks.

The friction coefficient of a lipstick applied on an artificial skin (urethane) was measured using a Slipping Tester HEIDON-14 (HEIDON Co.). The stick (1cm in diameter) was loaded to 200 g applied at 5 m/min. The gloss value of a lipstick was measured using a Spectrometer GM-268 (Minolta Co.).

3. Results and Discussion

3-1. Hardness of the gel composed of n-paraffin wax and commercial branched paraffin wax

Adding a small amount of b-PW to n-PW has been the most commonly used method to increase gel hardness. Figure 1 shows the relationship between gel hardness and the proportion of b-PW. The total amount of wax in the gel was kept at 20 wt.%, whereas the mixture ratio of the b-PW was varied. Gel hardness increased with addition of b-PW (less than 20 wt.%), and then *decreased with increasing amounts of b-PW.*

3-2. Properties of wax crystals in the gel consisting of n-paraffin wax and commercial branched paraffin wax

To clarify the mechanism behind gel hardness variation between n-PW and b-PW mixtures, we investigated the crystallinity and crystal size of the wax in the gel.

Firstly, the crystallinity was estimated from an X-ray diffraction pattern of the gel. As shown in Figure 2, the crystallinity decreased with increasing amounts of b-PW. Next, the crystal size was measured from SEM images. Size decreased when the proportion of b-PW was less than 20 wt.%, and in this region the gel hardness increased. On the other hand, the size remained constant with further increase (>20 wt.%).

When crystal size becomes smaller, the connecting points of each wax crystal are increased. This makes the gel harder.

These findings suggest that variation of gel hardness is caused by the competing effects of decreasing crystal size making the gel harder, and decreasing crystallinity making the gel softer.

3-3. Molecular design of a new branched wax and gel hardness control

Considering this result, it was assumed that a harder gel could be obtained if it were possible to make the crystal size smaller without decreasing crystallinity.

Therefore, we developed a new branched wax for the control of oil-wax gel hardness, B is(polyethylenyl)-tetramethyldisiloxane (ESE). As shown in Scheme I, the ESE molecule is composed of a central tetramethyldisiloxane unit (branch unit) with polyethylene units at both ends. The branch unit may suppress crystal growth and the end units are expected to prevent the wax crystallinity from decreasing during the process of crystallization.

Hardness variations of the gels composed of n-PW and ESE are shown in Figure 3.

In the range where the ratio of ESE to the total amount of wax was 5 wt.% to 40 wt.%, the gel hardness increased dramatically. It reached 14.5×10^5 Pa at 40 wt.%, and this state of gel hardness was maintained in the mixture range from 40 wt.% to 80 wt.% ESE. This result indicates that the gel mixed with ESE became remarkably harder and more stable over a wider mixture range than the b-PW mixtures.

3-4. Properties of wax crystals in the gel containing ESE

Properties of the wax crystals in the gel composed of n-PW and ESE were examined using the same methods as for the b-PW gels.

The SEM image of the 'oil-free gel' structure is shown in Figure 4. The size of the wax crystals and the crystallinity in the gel are indicated in Figure 5. The size of wax crystals decreased remarkably (to about 10 µm) on addition of ESE (20 wt.%) and remained stable over the mixture range above 20 wt.%. Further, the crystallinity was stable for the entire mixture range, in contrast to the behavior of b-PW gels.

From these results, we assume that the drastic increase in gel hardness was due to smaller crystals without a decrease in crystallinity.

The internal structure of the ESE crystal was investigated.

The vertical sectional image (long spacing image) of the ESE crystal was observed by TEM. As shown in Figure 6, interestingly, the ESE crystal had a perfect multilayer structure composed of crystalline layers (unstained) and amorphous layers (stained).

This indicates that ESE crystallizes regularly, despite the fact that the molecule contains a bulky branched unit (disiloxane) in the middle.

The mixed crystal consisting of ESE and n-PW (1:1) was subsequently investigated. In this mixture, the size of the crystal became smaller whilst retaining its crystallinity, and the gel hardness was increased drastically.

The XRD pattern of the mixed crystal showed a single phase and was shifted to a pattern intermediate between the patterns of n-PW (orthorhombic) and ESE (Figure 7).

From this result, the mixed crystal of n-PW and ESE is considered to form a solid solution in the ratio (n-PW: ESE=1:1).

3-5. Application of ESE in lipsticks

The question of whether ESE increases the hardness of lipstick was investigated.

Model lipsticks with wax content ranging from 12 wt.% to 20 wt.%, were prepared and evaluated. As expected, the hardness of the lipstick dramatically increased when ESE was used (Figure 8). It is well known that the gloss and smoothness are reduced by high wax content. Using ESE, however, it is expected that the wax content in lipsticks can be decreased drastically, preserving gloss and smoothness, without degrading stick hardness.

Thus, lipstick containing ESE (Sample 1) was compared with lipstick lacking ESE (Sample 2) with regard to application properties (the gloss value and the frictional coefficient). These two lipsticks were of approximately the same hardness (Figure 8).

As shown in Table II, the gloss value of applied lipstick Sample 1 was found to be significantly higher than that of Sample 2. In addition, the frictional coefficient of Sample 1 was found to be lower, meaning that it has a smoother feel than Sample 2.

4. Conclusion

The relationship between gel hardness and crystal properties, crystal size and crystallinity, was examined using oil-wax gels containing n-PW and b-PW. Harder gels could be obtained if crystal size can be reduced without decreasing crystallinity. Considering this result, we have developed a new branched wax (ESE) to improve the gel hardness. ESE molecules are composed of a central tetramethyldisiloxane unit (branch unit) with polyethylene units at both ends. As expected, when ESE was added to n-PW, the wax crystals obtained became smaller without decrease in crystallinity. Consequently, the gel hardness was dramatically increased. The total amount of wax in the lipstick could thus be reduced by 30% without spoiling the stick toughness. Therefore, glossier application and smoother texture could be achieved.

This unique function of ESE can be used in practice to improve the qualities of various cosmetic products such as lipsticks.

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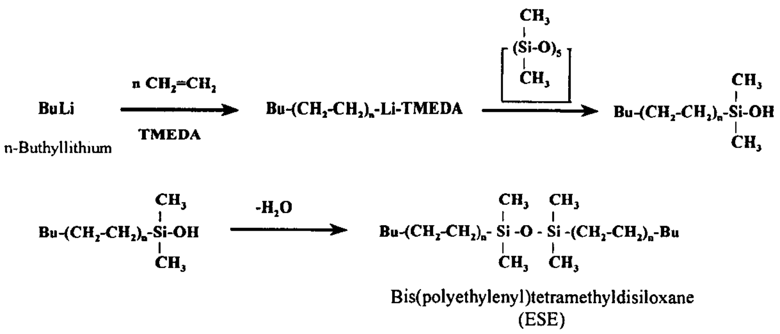
Table I Formula of model lipsticks

Sample No.	Sample 1 (Containing ESE)	Sample 2 (Not containing ESE)
Formula (wt.%)		
Solid Paraffin	5	5
ESE	5	-
Wax mixture	2	11
Oil mixture	80	76
Pigments	8	8



Scheme I Synthesis of Bis(polyethylenyl)tetramethyldisiloxane (ESE) by anionic living polymerization

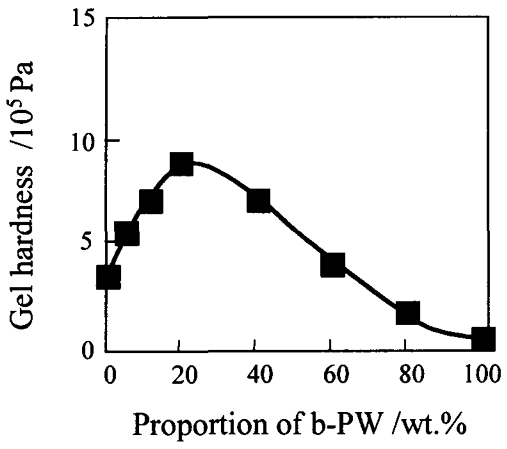


Fig. 1 Relationship between the gel hardness and proportion of b-PW among waxes.
wax (n-PW and b-PW) /oil = 20/80

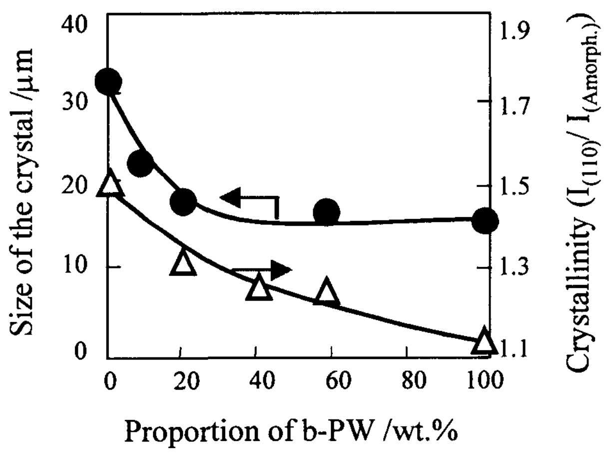


Fig. 2 Relationship between properties of wax crystals and proportion of b-PW among waxes.
● :wax crystal size, Δ :crystallinity

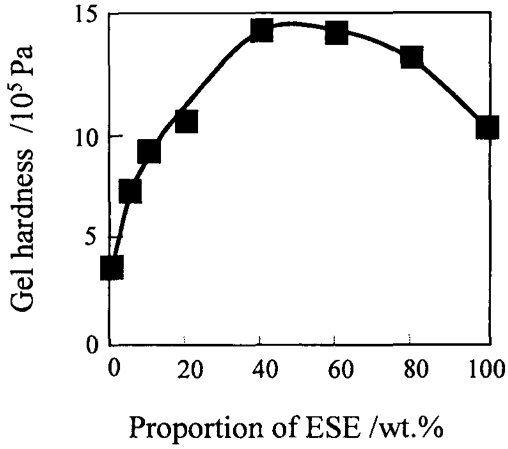


Fig. 3 Relationship between the gel hardness and proportion of ESE among waxes.
wax (n-PW and ESE) /oil = 20/80

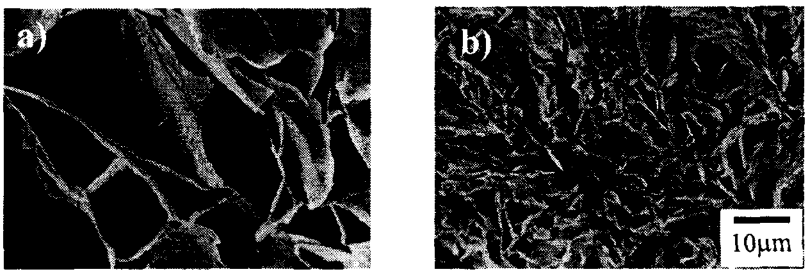


Fig. 4 SEM image of oil wax gel structure after removing oil.
Waxes are a) n-paraffin wax, b) n-paraffin wax / ESE = 60/40

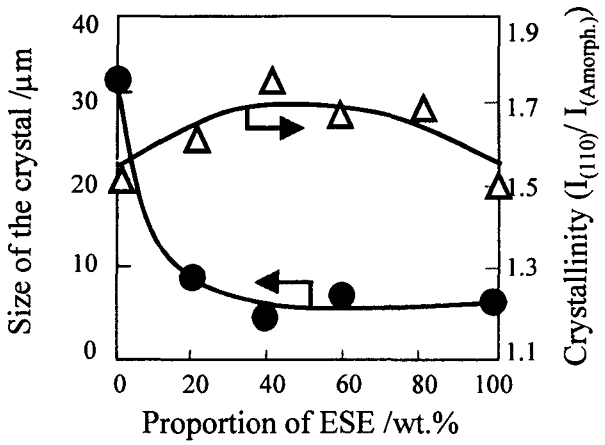


Fig. 5 Relationship between properties of wax crystals and proportion of ESE among waxes.
●:wax crystal size, Δ:crystallinity

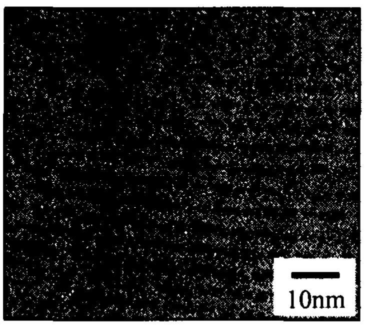


Fig. 6 TEM image of the vertical section of ESE crystal.

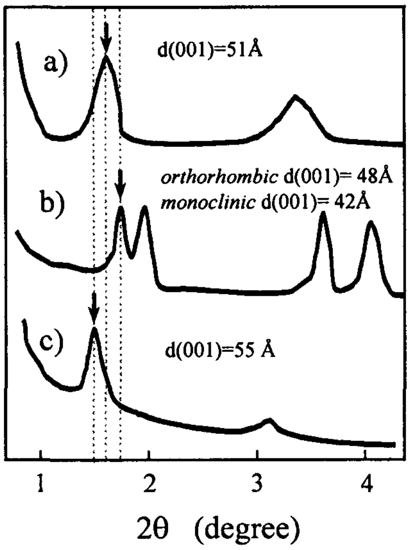


Fig. 7 XRD patterns of wax crystal

a) n-paraffin wax/ ESE= 1/1
b) n-paraffin wax
c) ESE

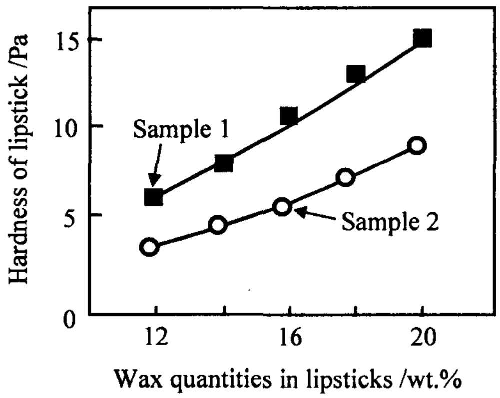


Fig. 8 Relationship between the wax quantities in lipsticks and their hardness
■ :containing ESE, O :not containing ESE

Table II Properties of applied lipstick on artificial skin

	Wax amount in lipsticks (wt.%)	Application gloss (%)[1]	Frictional coefficient when applied
Sample 1 (Containing ESE)	12	120	0.27
Sample 2 (Not containing ESE)	16	100	0.38

1) The relative value based on Sample 2.