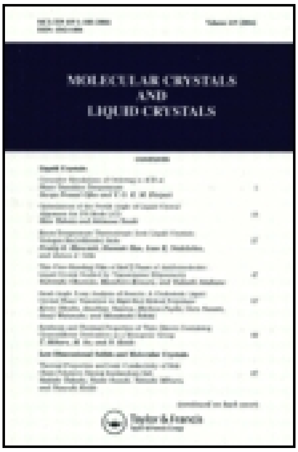

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The Properties of Oil–Wax Gels With Changing Lattice Structure of Wax Crystal

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The objective of this study was to investigate the relationship between the lattice structure of ceresin wax and different wax mixtures and the glossiness of oil–wax gels. Recently, visual factors such as the glossiness of skin are generally known as the words to express the beauty. The mechanism of glossiness has been suggested to understand the changes that occur in the lattice structure of the wax crystal when they are forming gels and also the effects of the nature of solvent. The present work investigates the relation between the lattice structure of the wax crystal and the glossiness of oil–wax gels obtained from ceresin and microcrystalline wax as well as of the gels formed by different waxes in solvent. The addition of branched wax to ceresin tended to form loose lattice structure of wax crystal, resulting in the high glossiness of oil–wax gels. However, the addition of n-paraffin wax to ceresin tended to form dense lattice structure of the wax crystal, leading to the low glossiness of oil–wax gels. The rheological transition behavior was also discussed as a function of the ratio of wax to ceresin.

Keywords Branched wax; glossiness; lattice structure; oil–wax gel; wax crystal

Introduction

Waxes, or long-chain hydrocarbons, may be obtained naturally from animals, vegetables, and mineral waxes, or may be synthesized such as paraffin wax, microcrystalline wax, synthetic wax, polyethylene, ceresin, candelilla wax, carnauba wax, and bees wax [1–8]. Petroleum waxes are complex mixtures of high molecular weight saturated hydrocarbons, predominantly paraffins, in the approximate range of C_{18}–C_{65}. Normally, those petroleum waxes are composed of principally n-alkanes that crystallize in large and flat plates, and hence are macrocrystalline and called as paraffin waxes. High molecular weight waxes with long side chain crystallize in tiny microscopic needles and are generally called microcrystalline waxes [2]. The physical properties of the waxes, e.g., their solubility in organic solvents and defined melting point, suggest a crystalline order, which has, however, not yet been generally proved for all types of waxes. In most waxes the molecules are packed in a characteristic order, which results in an orthorhombic symmetry. Certain wax compounds crystallize preferentially in a triclinic order, and exhibit a hexagonal structure often at a high temperature just below the melting point [9–11].

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Oil–wax gel is the oily solid composed of liquid oils and crystalline solid oils, which is widely applied to variety of cosmetics, such as lipsticks [6,12,13]. Extensive research has been carried out to investigate the lattice structure of wax mixture in pure solvents (hydrocarbones) [2–8]. Different species of waxes forming solid state greatly influence the surface properties, which depend on crystal conformation, crystal size, and the degree of crystallinity of oil–wax gel [14]. We investigate here the morphological and physical properties of oil–wax gels by changing lattice structure of wax crystal. The control of glossiness is one of the most important techniques in improvement of the cosmetics quality. Visual factors such as the glossiness of skin are generally known as the words to express the beauty. Although, the beauty is evaluated by only a visual sensory method, it is considered that the visual factors are dependent upon the optical reflection on the skin surface [15]. The mechanism of glossiness has been suggested to understand the changes that occur in the lattice structure of wax crystal when they are forming oil–wax gels as well as the effects of the nature of solvent. Generally, branched wax has been developed for the control of the hardness of oil–wax gels. Addition of small amounts of commercial branched microcrystalline wax to n-paraffin wax has been commonly used to increase gel hardness. However, gel hardness is very sensitive to the quantity of branched wax, and the gel obtained is not always hard enough for practical use [6,15]. It is considered that the change of gel hardness is related to the lattice structure of wax mixture.

In this study, we observed the influence of branched chain wax (microcrystalline wax) and linear chain wax (n-paraffin wax) between the lattice structure of wax crystal and morphological and physical properties on oil–wax gels [16,17].

Experimental

Materials and Methods

Oil–wax gels were prepared through the mixing process of ceresin (Nikkorica, Japan), which is a white to yellow waxy mixture of hydrocarbons obtained by purification of ozokerite, branched microcrystalline wax (Strahl & Pitsch, NY), which is a wax derived from petroleum and characterized by the fineness of its crystals in contrast to the larger crystals of paraffin wax, n-paraffin wax (Myungdo Industry, Korea), which is a solid mixture of hydrocarbons obtained from petroleum characterized by relatively large crystals, and polyglyceryl-2 triisostearate (Nisshin Oillio, Japan, Cosmol 43), which is the trimester of isostearic acid. The appropriate amounts of oils and waxes were heated to 100°C and stirred to form a homogeneous solution. The mixture was poured into a mold and allowed to stand at room temperature for over 12 h (Table 1).

Three kinds of waxes were characterized by differential scanning calorimeter (DSC) measurement, as shown in Fig. 1. Ceresin and n-paraffin wax displayed narrow melting

Table 1. The composition of oil–wax gels with the change of wax ratio

	A	B	C	D	E	F	G	H	I	J	K	L	M	N
Ceresin	15	14	13	12	14	12	10	8	6	14	12	10	8	6
Branched microcrystalline	–	–	–	–	1	3	5	7	9	–	–	–	–	–
n-Paraffin	–	–	–	–	–	–	–	–	–	1	3	5	7	9
Cosmol 43	85	86	87	88	85	85	85	85	85	85	85	85	85	85

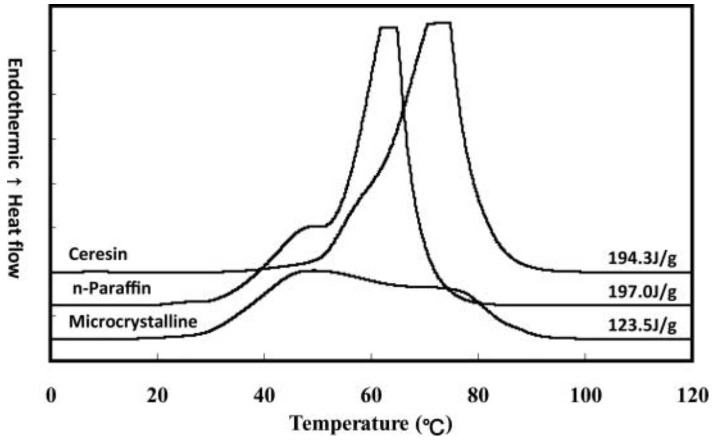

Figure 1. The DSC thermograms of ceresin, n-paraffin, and branched microcrystalline wax.

peaks and high heat capacity, but branched microcrystalline wax displayed a broad melting peak and low heat capacity relatively.

Measurements

DSC measurements were carried out with a Hart DSC-II (CSC 4100, Calorimetry Sciences Co., Lindon, Utah) equipped with a thermal analysis data system for baseline correction, transition temperature, and calculation of the transition heat. Samples were heated up to 100°C then cooled down to 0°C by 2°C min^{-1} of cooling rate under a constant flow of nitrogen gas [18,19].

The rheological measurements were performed with a USD 200 Universal Dynamic Spectrometer (Paar Physica, Ostfildern, Germany) using parallel plate geometry (truncated radius 5 mm). All samples were prepared in a square stainless mold (40 mm × 40 mm × 5 mm) and kept at 25°C for one week. Samples were mounted on parallel plates with the gap size of 0.5 mm. Test was performed at least in duplicate using fresh samples for each run. Data were analyzed using the manufacturer's software. Oscillatory experiments were performed under very low periodic shear strains, 0.00001–10, to investigate the internal structure of the product. The resulting parameter is the storage modulus G' (expressed in Pa), which represents the elastic character of the product. The hardness of oil–wax gels was measured on a Fudoh Rheometer (RT-35005D, Rheotec Co., Tokyo, Japan) with adapter #30 cutting machine at 25°C. Samples were prepared in lipstick mold with 12 mm diameter. The glossiness of oil–wax gels was observed with VG 2000 gloss meter (Nippon Denshoku, Tokyo, Japan) and samples were prepared in Vitro-Skin (IMS, Inc., Portland, Maine) by rubbing oil–wax gels uniformly just before the test. The change of lattice structure of wax matrix was analyzed by using scanning electron microscope (SEM) (FE-SEM S-4800, Hitachi, Japan).

Results and Discussion

Physical Properties of Oil–Wax Gel

The hardness of the oil–wax gels consisting of ceresin wax, branched wax or n-paraffin wax, and oil is shown in Fig. 2. The sample labels are mentioned in Table 1. The hardness

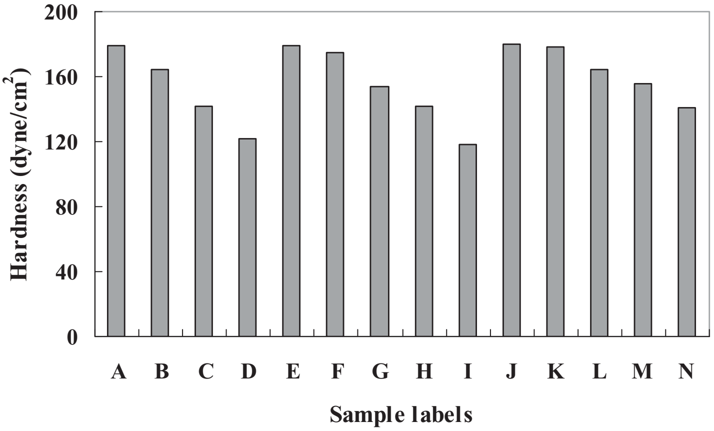

Figure 2. The hardness of oil–wax gels depending on the amount or ratio of ceresin, n-paraffine, and branched microcrystalline wax.

of the oil–wax gels was proportionally decreased with decreasing ceresin wax content [Figs. 2(a)–(d)]. The addition of branched wax [Figs. 2(e)–(i)] and n-paraffin wax [Figs. 2(j)–(n)] to ceresin oil–wax gels tends to decrease the hardness of oil–wax gels. This result is contradictory to the Shibata's work [20]. The difference is coming from the different composition of the mixed wax and melting point. In general, the range of wax content is 15%–30%. In case of Shibata's study, they used branched wax with higher melting point (90°C) compared to the n-paraffin wax with lower melting point (70°C). It resulted in condition such that the addition of branched wax increased gel hardness because of the monocrystal phase. In this work, however, we used branched wax with lower melting point compared to the ceresin wax with higher melting point, which is illustrated in Fig. 1. This is why the addition of branched wax decreased gel hardness due to the low crystallinities, as will be shown later (in Fig. 5). This result agrees with Yoshida's study related to the change of wax crystal. Yoshida et al. [15] investigated the relationship between the gel hardness and the composition of the branched wax in the wax mixtures. They reported that the crystal size and crystallinity were decreased with increasing the composition of the branched wax in the wax mixtures. The crystallinity was reduced with decreasing the hardness of the oil–wax gel.

The Lattice Structure of Oil–Wax Gel

Figure 3 shows the SEM images of wax matrixes, which consisted of pure ceresin and branched wax (or n-paraffin wax). The lattice structure of wax crystal surrounding the oil became more clearly observed as the composition of the branched wax relative to ceresin is larger. However, the lattice structure of wax crystal is not changed significantly when the ratio of n-paraffin wax to ceresin increases. Loose lattice structure of wax crystal surrounding oil was formed when the branched wax was added, which interfered with the formation of the dense lattice structure of the ceresin wax crystal. This loose lattice structure of wax crystal resulted in the decreased hardness of oil–wax gels owing to the reduction of crystallinity, as already shown in Fig. 2. When n-paraffin wax was added, the hardness of oil–wax gels was slightly decreased, though the dense lattice structure of wax crystal was

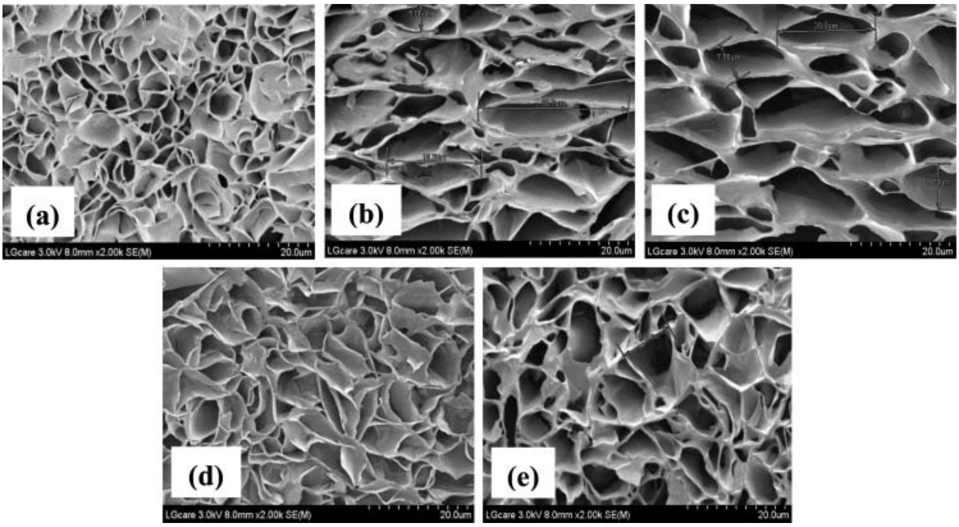

Figure 3. SEM images of oil–wax gels after extracted oil (a) A, (b) F, (c) H, (d) K, (e) M.

not changed. It meant that n-paraffin wax did not interfere much with the formation of the dense lattice structure of the ceresin wax crystal compared with the branched wax.

This lattice structure of wax crystal surrounding oil is important to the glossiness of oil–wax gels. The glossiness is related with a kind (or amount) of oil in wax matrixes. For the loose lattice structure of wax crystal, a large amount of oil is included, whereas for the dense lattice structure of wax crystal, a small amount of oil is included, as shown in Fig. 3. Figure 4 shows the glossiness of oil–wax gels as a function of wax crystal. The glossiness of oil–wax gels was slightly increased with decreasing the amount of ceresin and increasing the ratio of n-paraffin wax to ceresin. However, the glossiness of oil–wax gels dramatically increased when the amount of the branched wax over 3% was mixed to ceresin. This is caused by the lattice structure of oil–wax gels. The SEM images in Fig. 3 hint that branched wax might contribute to form loose lattice structure of wax crystal. The loose lattice structure of the wax crystal tended to spread a large amount of oil to the vitro

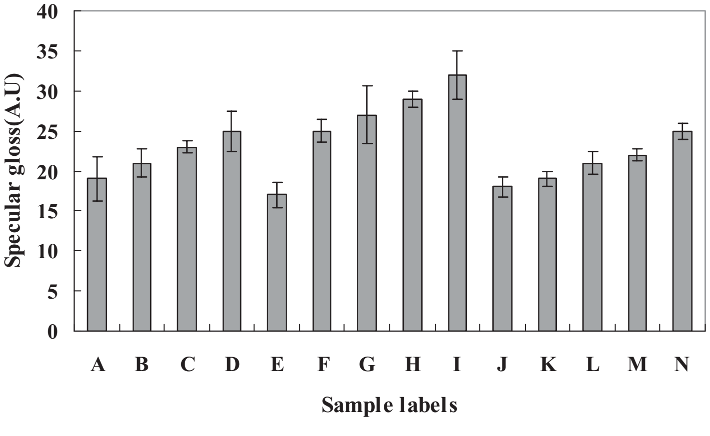

Figure 4. The glossiness of oil–wax gels depending on the change of lattice structure.

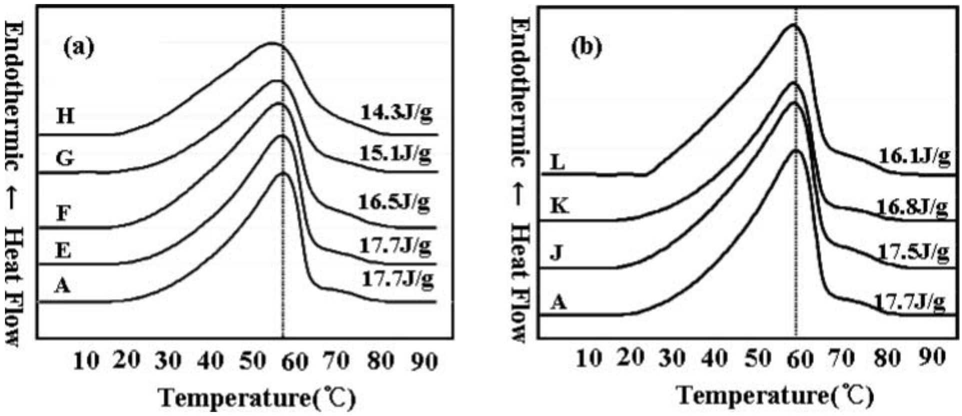

Figure 5. The DSC thermograms of ceresin/microcrystalline wax/cosmol 43 ternary systems (a) and ceresin/n-paraffine wax/cosmol 43 ternary systems (b) after storage at 25°C and heating rate of 2°C min^{-1}.

skin when oil–wax gels were collapsed by external force, while the dense lattice structure of the wax crystal tended to spread a small amount of oil. A large amount of oil increased the glossiness of oil–wax gels because the glossiness of the oil–wax gels was proportional to the oil contents.

Takeo et al. [6] investigated the relationship between the hardness of oil–wax gels and the surface structure of the wax crystals. They explained that the hardness of oil–wax gels depended on the polarity of oils and wax crystal. Gel hardness was increased when (1) the polarity of oils was higher, (2) low compatible waxes were applied in both wax systems, (3) the surface of crystal was rough, and (4) wax crystals have more steps on their surface [6]. The addition of branched wax to ceresin shifted the peak of melting point to low temperature and decreased heat capacity, as shown in Fig. 5(a). Heat capacity was greatly decreased as the branched wax over 3% was applied. It meant that the branched wax was likely to decrease the crystallinity of ceresin and increase the compatibility of both waxes. Therefore, the peak was getting broader as the ratio of the branched wax to ceresin increased, which influenced the formation of lattice structure of the wax crystal and the glossiness of oil–wax gels. On the other hand, peak broadening and peak shift hardly occurred when the n-paraffin wax was applied to ceresin, as shown in Fig. 5(b). n-Paraffin wax did not affect the lattice structure of ceresin, when compared with branched wax, because n-paraffin wax and ceresin have a similar structure, i.e., straight chain structure. The change of crystallinity and lattice structure of wax crystal could influence the rheological behavior, and thus the surface structure of oil–wax gels.

Rheological Behaviors of Oil–Wax Gel

Figure 6 shows the change of storage modulus (G') as a function of shear strain in the oil–wax gels. It exhibited two or three steps of the storage modulus (G') transition over the entire strain ranges [21]. It appeared that the first step transition occurred dramatically on increasing the ratio of the branched wax to ceresin [Fig. 6(a)], while the first step transition was marginal, even if the ratio of the n-paraffin wax to ceresin was increased [Fig. 6(b)]. Branched wax tended to form loose lattice structure of oil–wax gels, while n-paraffin wax tended to form dense lattice structure of oil–wax gels, as shown in Fig. 3. The first step

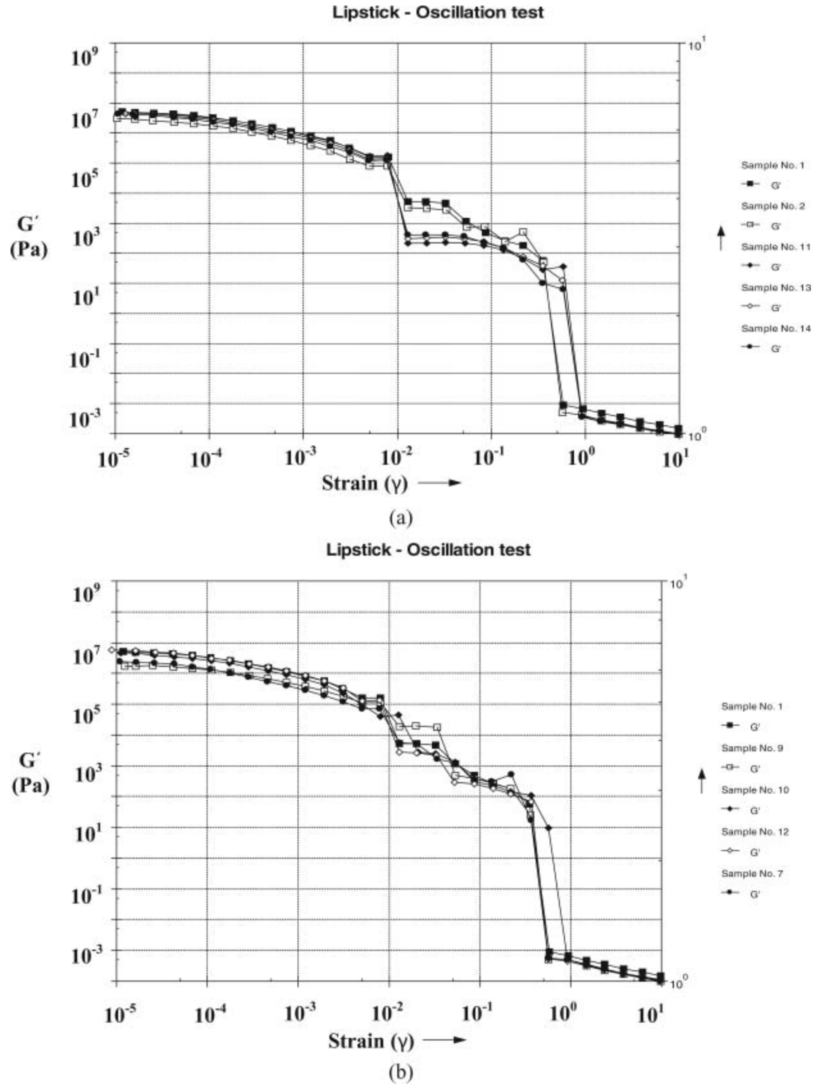

Figure 6. The storage modulus (G') as a function of shear strain (γ) for oil–wax gels (a) A (■), E (□), F (●), G (□), H (□), and (b) A (■), J (□), K (●), L (□), M (□).

transition was related to the loose lattice structure of oil–wax gels, and the glossiness of oil–wax gels was increased with increasing the first step transition, because the loose lattice structure of the wax crystal including a large amount of oil was easily collapsed at lower strain. In case of dense lattice structure of the wax crystal including a small amount of oil, even if lattice structure was collapsed by lower strain, the first step transition was marginal, because neighboring lattice structure supported the dense lattice structure of the wax matrix.

Conclusions

The lattice structure of wax crystal surrounding oil is important to the glossiness of oil–wax gels. The addition of branched wax to ceresin tended to form loose lattice structure of wax crystal, resulting in the high glossiness of oil–wax gels. However, the addition of n-paraffin wax to ceresin tended to form dense lattice structure of the wax crystal, leading to the low glossiness of oil–wax gels. The rheological measurements showed that first step transition occurred dramatically as the ratio of branched wax to ceresin increased, while the first step transition was marginal, even though the ratio of the n-paraffin wax to ceresin was increased.

Acknowledgments

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