The Internal Structure and Tribology of Calcium Lauroyl Taurate

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Calcium lauroyl taurate ($C_{11}H_{23}CONH(CH_2)_2SO_3 \cdot 0.5Ca$, CaLT) was synthesized, and the internal structure and tribology were studied. The powder of CaLT is a plate type crystal whose structure is lamellar at room temperature. When the powder is applied to an artificial skin, the frictional coefficient is lower than that for other solid lubricants. Such a high lubricity is caused by disintegration of the powder aggregates, cleavage of the lamellar layers, and deformation of the powder particles.

Powders which induce smooth or soft feelings are important as cosmetic materials.[1] There are many physical properties which affect an evaluation of 'sensuousness' when touched, but the causes of this relationship are not well understood. However, low frictional resistance is necessary to obtain a smooth feeling according to cosmetic chemists. Surface-active agent metal salts and their related compounds, i.e. zinc stearate (ZnST), lauroyl lysine (LL) and sodium-zinc salt of cethyl phosphate (NZCP), are suitable lubricants for cosmetics because they show low frictional resistance due to disintegration of the powder aggregates, cleavage of the lamellar layers and deformation of the powder particles when they are applied to skin.[2,3]

In a search for more lubricious materials than those currently in use, we have synthesized calcium lauroyl taurate (CaLT, Figure 1).[4] In this work, the internal structure of CaLT was assessed by X-ray diffraction (XRD) and atomic force microscopy (AFM), and its tribology, especially the lubricity, was evaluated.[5,6]

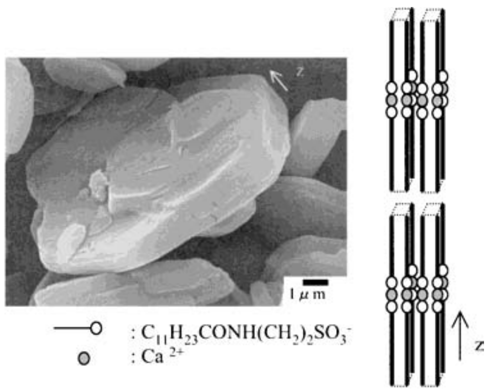

Figure 1. A SEM image and a crystal structure of CaLT.

The physical properties and the internal structure of CaLT are as follows: CaLT is a white powder with a high fluidity (angle of repose=53°). The particle size is 8 μm, with a plate-like shape. The crystal structure of CaLT was studied using XRD. Strong diffraction peaks which are assigned to the (100), (200) and (300) crystal faces were observed at 2.3, 4.6 and 6.9°. The XRD pattern indicates that the crystal is a lamellar structure with a long spacing of 37.6 Å. In addition, some weak diffraction peaks were observed at 20–30°. If these peaks are attributed to diffractions by short axis faces, the spacing is 3–4 Å. An AFM image of the CaLT surface (Figure 2) reveals an ordered pattern with an interval of 3–4 Å. The pattern is consistent with alkyl chains ordered in a lamellar structure.[7] The results of XRD and AFM indicate that CaLT is a lamellar molecular crystal with laminated layers of linear molecules (Figure 1).

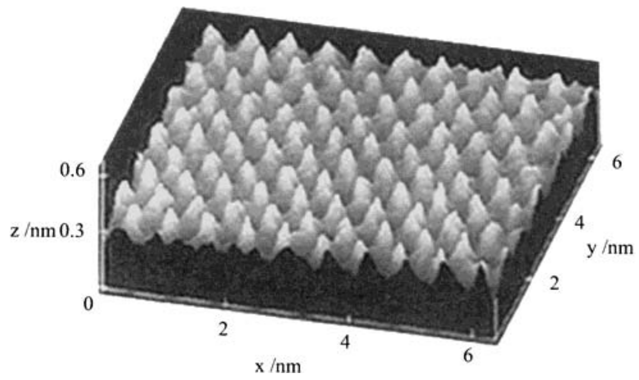

Figure 2. An AFM image of CaLT surface.

The lubricity of CaLT and solid lubricants was evaluated (Figure 3).[6] When CaLT was applied to an artificial skin, the frictional coefficient was 0.27, lower than that for other solid lubricants used in cosmetic materials. Moreover, stick-slips, i.e. periodic changes of the frictional resistance, were not observed when CaLT was applied to an artificial skin under a low shear rate ($1.2 \cdot 10^{-4}$ m s^{-1}), while such stick-slips were observed when inorganic powders were applied (Figure 4). The "stick" is due to the high static friction between two faces, and the "slip" to the low kinetic friction during the slip.[8] The changeless profile on the application process indicates that the difference between the static and the kinetic frictions for CaLT is smaller than that for the inorganic powders.

Here we postulate a mechanism of lubricity. In general, it is recognized that lamellar compounds induce a lowering of frictional resistance due to cleavage of lamellar layers.[9] We predict that the lubricity of CaLT is caused not only by cleavage, but also by other factors, such as disintegration of the powder aggregates and deformation of the powder particles, as a SEM image showed that CaLT was deformed to a thin layer when applied to an artificial skin. The thin layer covers projections on the artificial skin and lowers the frictional coefficient.

The frictional coefficients indicate that CaLT is more lubricious than other surface-active agent metal salts, i.e. ZnST and NZCP. The mechanism is not yet clear, but we hypothesize that the difference is a result of the regularity of the crystal

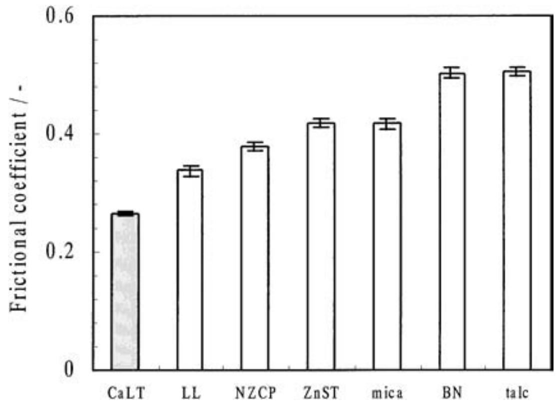

Figure 3. Frictional coefficients of CaLT and other powder lubricants (rubbing rate=$3.3 \cdot 10^{-2}$ m s^{-1}).

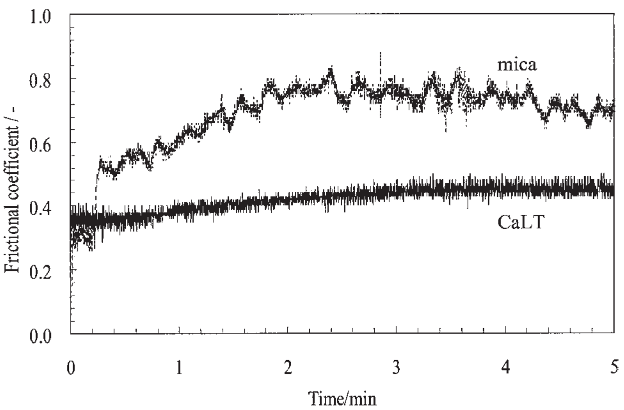

Figure 4. Change of frictional coefficients on application process of CaLT and mica (rubbing rate=$1.2 \cdot 10^{-4}$ m s^{-1}).

structure. CaLT crystals have high regularity due to intermolecular interactions, i.e. van der Waals interactions between alkyl chains, electrostatic interactions between Ca^{2+} ion and sulfonate groups and hydrogen bondings between taurate moieties. This higher regularity should induce smoother lamellar surface and higher lubricity than for other surface-active agent metal salts. Attempts to test this hypothesis by means of XRD and thermodynamic measurements are ongoing.

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References and Notes

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4 CaLT was synthesized as follows: taurine (Wako Pure Chemical Ind., Ltd., first grade, 504.3 g, 4.03 mol) was dissolved in 4259 g of a mixture (86 : 14, wt/wt) of deionized water and isopropyl alcohol (Katayama Chemical, Inc., reagent grade, IPA) to which was added 163.6 g of sodium hydrate. Lauric acid chloride (Tokyo Kasei Kogyo Co., Ltd., reagent grade, 799.4 g, 3.66 mol) and 304.0 g of 48% aqueous sodium hydrate solution was dropped to the taurine solution for 1 h at 40°, then the reaction mixture was stirred for 1 h at 40 °C to obtain sodium lauroyl taurate. After adding 40 g of 35% hydrochloric acid, 20% of an aqueous calcium chloride solution (Wako Pure Chemical Ind., Ltd., reagent grade, 1113.3 g, 2 mol) was added, and the reaction mixture stirred for 1 h at 40 °C. The white precipitate was filtered and the cake was washed by deionized water and IPA, then dried (yield: 85%). Anal. Found: C, 51.67; H, 8.95; N, 3.84; S, 9.38; Ca, 5.70%. Calcd for $C_{28}H_{56}O_8N_2S_2Ca$: C, 51.51; H, 8.64; N, 4.29; S, 9.82; Ca, 6.14%. ^{1}H-NMR(D_2O/d^{8}IPA, 1 : 1): 0.88(t, 3H, CH_3); 1.27(s, 16H, CH_2); 1.59(s, 2H, CH_2); 2.21 (t, 2H, CH_2); 5.33(s, 2H, CH_2); 3.02(t, 2H, CH_2); 3.33(t, 2H, CH_2). IR(KBr,/cm^{-1}): 3311(NH); 2954, 2919, 2850(CH); 1639(CO-N); 1196, 1169(SO_3^-). The physical properties of CaLT are as follows: specific gravity, 1.25 g cm^{-3}; bulk specific gravity, 0.37 g cm^{-3}; specific surface area (BET method), 1.2 m^2 g^{-1}; pH for the powder dispersed in water (CaLT/water, 91 : 9, wt/wt), 5.7; solubility, insoluble for water. CaLT satisfies safety criterions such as acute toxicity, mutagenicity, eye irritation and skin irritation.
5 XRD was performed using Rigaku Co. RINT 2500 V with CuKα as the X-ray source. An AFM image in contact mode was obtained using a Digital Instruments Nanoscope II scanning probe microscope. Particle size was measured by a Horiba LA-920 laser scattering particle distribution analyzer with the powder dispersed in ethanol. Angle of repose and bulk specific gravity were measured using a Seishin Multi Tester MT-1000. Specific gravity and specific surface area were measured by Shimadzu Accupyc 1330 micromeritics and Quantachrome Autosorb-1 automatic volumetric sorption analyzer, respectively.
6 NZCP was prepared by a literature method.[3] Mica (Yamaguchi-mica Co., Y2300, ϕ5 μm), talc (Yamaguchi-mica Co., KK500s, ϕ10 μm), boron nitride (Toray Industries, Inc., T-BN-C, ϕ10 μm), lauroyl lysine (Ajinomoto Co., Inc., amihope LL, ϕ10 μm) and stearic acid (Seido Chemical Co., ϕ1 μm) were purchased their commercial products. Frictional coefficients were measured using a Heidon 14DR surface property tester when the powder (200 mg) was rubbed under a weight of 200 g on 9 cm^2 of an artificial skin (urethan, Okamoto OK sheet).[3]
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